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ABSTRACT

This monograph consists of a text, a guide to the experiments for students, and a guide to the experiments for instructors. The text is intended to provide continuity to relate the experiments to one another and to provide some mathematical basis for analysis of the various phenomena observed. Only the five experiments performed in the student testing program of the conference are included in the student guide. However, the instructor's guide contains the descriptions for 23 experiments, most of which have been successfully tested. The text consists of four chapters: Pressure and Temperature as Properties of Matter; Equations of State; Heat; and Phase and Phase Diagrams. (PR)

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What Can the Matter Be?

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JACK A. SOULES

New Mexico State University

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GENERAL PREFACE

This monograph was written for the Conference on the New Instructional Materials in Physics, held at the University of Washington in the summer of 1965. The general purpose of the conference was to create effective ways of presenting physics to college students who are not preparing to become professional physicists. Such an audience might include prospective secondary school physics teachers, prospective practitioners of other sciences, and those who wish to learn physics as one component of a liberal education.

At the Conference some 40 physicists and 12 filmmakers and designers worked for periods ranging from four to nine weeks. The central task, certainly the one in which most physicists participated, was the writing of monographs.

Although there was no consensus on a single approach, many writers felt that their presentations ought to put more than the customary emphasis on physical insight and synthesis. Moreover, the treatment was to be "multi-level" --- that is, each monograph would consist of several sections arranged in increasing order of sophistication. Such papers, it was hoped, could be readily introduced into existing courses or provide the basis for new kinds of courses.

Monographs were written in four content areas: Forces and Fields, Quantum Mechanics, Thermal and Statistical Physics, and the Structure and Properties of Matter. Topic selections and general outlines were only loosely coordinated within each area in order to leave authors free to invent new approaches. In point of fact, however, a number of monographs do relate to others in complementary ways, a result of their authors' close, informal interaction.

Because of stringent time limitations, few of the monographs have been completed, and none has been extensively rewritten. Indeed, most writers feel that they are barely more than clean first drafts. Yet, because of the highly experimental nature of the undertaking, it is essential that these manuscripts be made available for careful review

by other physicists and for trial use with students. Much effort, therefore, has gone into publishing them in a readable format intended to facilitate serious consideration.

So many people have contributed to the project that complete acknowledgement is not possible. The National Science Foundation supported the Conference. The staff of the Commission on College Physics, led by E. Leonard Jossem, and that of the University of Washington physics department, led by Ronald Geballe and Ernest M. Henley, carried the heavy burden of organization. Walter C. Michels, Lyman G. Parratt, and George M. Volkoff read and criticized manuscripts at a critical stage in the writing. Judith Bregman, Edward Gerjuoy, Ernest M. Henley, and Lawrence Wilets read manuscripts editorially. Martha Ellis and Margery Lang did the technical editing; Ann Widditsch supervised the initial typing and assembled the final drafts. James Grunbaum designed the format and, assisted in Seattle by Roselyn Pape, directed the art preparation. Richard A. Mould has helped in all phases of readying manuscripts for the printer. Finally, and crucially, Jay F. Wilson, of the D. Van Nostrand Company, served as Managing Editor. For the hard work and steadfast support of all these persons and many others, I am deeply grateful.

Edward D. Lambe
Chairman, Panel on the
New Instructional Materials
Commission on College Physics

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P R E F A C E

This monograph consists of three related parts. There is a "text," a guide to the experiments for students, and a guide to the experiments for instructors. The principle feature of the monograph is the set of experiments. The function of the text is to provide continuity to relate the experiments to one another and to provide some mathematical basis for analysis of the various phenomena observed. Only five experiments have been performed in the student testing program of the conference. Therefore, only five experiments are included in the student guide. The guide for instructors is more extensive. Many of the experiments have been constructed and tested, either during the conference or elsewhere. Preparation of these experiments is outlined in detail and they can be reproduced without difficulty. Another group of experiments has been planned and some design criteria stated. However, these have not been constructed and so some "bugs" may have to be exterminated before they are ready for student use. Finally, there are several experiments which have not been considered very carefully at all. They appear here only in the form of suggestions as to how one might do them.

A few of the experiments require sophisticated optical apparatus or other advanced techniques. Those experiments may be performed by the instructor if necessary. Films of the experiments may occasionally be substituted for the real experience and/or used as review material.

The use of the laboratory as a teaching method is relatively expensive and inefficient compared to reading a text or listening to a lecture. However, efficiency must not be measured only in terms of verbal recall. Laboratory learning has a way of continuing long after the formal experience has ended. As the student develops confidence in his ability to learn facts by observing apparatus he becomes capable of learning independent of teachers. It is on this premise that this monograph has been constructed. There is not a unique body of knowledge to be imparted through these pages. Many interesting and valuable phenomena have been omitted and those that have been included

have been selected to offer a set of experiences of increasing complexity. Hopefully, the student who works his way to the last experiment will be prepared to continue his education in formal courses in kinetic theory, solid state physics, physical chemistry, meteorology, metallurgy, and thermodynamics.

1 PRESSURE AND TEMPERATURE AS PROPERTIES OF MATTER

In these pages we are going to examine the properties and behavior of matter, the tangible, bulky stuff that surrounds us, flows past us, and bumps into us every day of our lives. We shall draw heavily upon experimental evidence in an attempt to see the pattern of behavior unfold just as our scientific ancestors saw it. We have the advantage, however, in that our experiments will be carefully selected. We can avoid many dark alleys and fruitless searches. Although our point of view here is going to be largely that of "physics," it will not mean a narrow restriction on the subject nor on the techniques of our investigation. In the ancient Greek academies the study of science was an outgrowth of the quadrivium: arithmetic, geometry, astronomy, and music. Gradually the study of the last three of these broadened into "natural philosophy." This tradition of the investigation of nature as a whole, not circumscribed by such modern boundaries as "physics," "chemistry," "metallurgy," "meteorology," continued well into the nineteenth century. It is only in recent years that the rapid growth of scientific knowledge has encouraged the separation of science into narrow and more specialized disciplines. But if we are to learn the secrets of matter it is important to avoid this narrowness, for we shall be obliged to draw upon the skills and insights of many sciences. We shall be interested in the properties of matter from whatever point of view offers an opportunity for insight and understanding.

When we set ourselves the task of understanding matter, we need to be more explicit about our goal. What does it mean to understand? Surely everyone understands what a gas is - it's like the air that blows against his face and through his hair. Everyone understands that a liquid flows and drips and is, perhaps, wet. And that a solid is rigid, immobile, springy, or hard. Each of these words is a part of our experience; each describes a property which is common to some of the objects we are considering. But is this "understanding? The ancient Greeks also "understood" matter. It was formed of four elements: air, fire, earth, and water. The properties of any substance could be explained in terms of combinations of those elements in different proportions. Myriads of combinations are possible, and the variety in the natural world reflects that diversity. Such understanding was a great achievement at its time but it no longer satisfies us. Since the four elements could be mixed in arbitrary amounts every real substance was describable by its special combination. No general rules were found to guide or restrict the choices. There was no way to understand why some combinations do <u>not</u> occur. Such a description of nature becomes little more than an exercise in rhetoric.

We need to take a moment to ask, "What constitutes understanding in science?" How will we know that our description of nature is an improvement over the Greek air, fire, earth, and water? Are there tests that one can use to examine the validity and utility of a scientific statement? We shall find that there are.

The descriptions of matter that we are going to develop in these pages are relatively modern. During the eighteenth and nineteenth centuries, great advances were made in organizing the properties of matter in terms of the quantities pressure, volume, and temperature. At the same time experiments on heat were performed and gradually the nature of heat became clear. An intimate relationship exists be-

tween heat and the properties of matter which requires that both be understood in a single context.[1]

Over the same period other natural philosophers were successful in applying the laws of force and motion to projectiles and other bodies. These laws had been developed by Newton to explain the motion of the planets under gravitational forces. In the nineteenth century the mechanical laws of particles were extended to include matter in bulk. Gases were described as collections of enormous numbers of tiny but finite particles and, soon after, the particle description was extended to liquids and solids.

Was this new understanding superior to the air-fire-earth-and-water of the Greeks? Yes, for several reasons, and from those reasons you will begin to see what we now mean by "understanding." First, the properties which were understood in terms of pressure, volume, and temperature could also be described in terms of particles, subject to forces and having velocities, and a complete "dictionary" exists for translating from one descriptive scheme to the other. This sort of thing happens frequently in physics. Alternate, apparently independent, systems grow up for describing a particular set of phenomena. Then new insight develops and it is seen that one system is a translation of the other into a new language. The description of matter in terms of its pressure, volume, and temperature emphasizes certain physical properties at the expense of others; nevertheless a direct correspondence exists between the pressure-volume-temperature description and the particle description.[2]

A second and perhaps more important reason for preferring the modern descriptions of matter is that they enabled us to successfully predict many properties of matter before they were observed. This is a very powerful test which modern science attempts to apply. The ability to predict the behavior of nature from laws we formulate is a strong argument that the "laws" are correctly formulated. The ancient scientists were so unsuccessful at predicting that they were not even convinced of the existence of "natural law." The belief that nature behaves in reproducible, unchanging ways is a relatively modern one. Prior to the time of Newton the right to be whimsical was reserved to God and nature and the proscriptions that a belief in natural law would impose were considered heretical. But science has both given strength to and drawn strength from the belief that nature is predictable, that she always responds in the same way when asked the same question.

Finally, modern descriptions of matter are inherently simple. Even though the Greeks did not succeed in discovering many laws of nature it was they who established the philosophical criteria for such laws. It is a tribute to their wisdom that it has proved possible over the years to develop a simple description of the behavior of matter. The idea of simple implies that a small number of concepts are involved; it is the search for these concepts that is the business of science.

In whatever scientific language or "representation" we choose to write it, our description of the behavior of widely different substances will be made in terms of a few fundamental concepts. The differences from substance to substance will appear in the quantity of one fundamental property or another which they have. This is very much like the Greek use of air-fire-earth-and-water except that we can assign fixed numbers to these properties and can even develop mathe-

[1] The phenomenological science of matter and heat is the branch of physics called thermodynamics.

[2] In recent years a third descriptive system has achieved some popularity in which some properties are described in terms of waves of vibration in a continuous medium. The new description is apparently equivalent to the old and is more convenient for describing certain properties. We might say that there are now three languages for discussing the properties of matter.

matical relations among the numbers.

There are many ways of selecting materials to examine and on which to base our first premises. Two in particular present themselves. We might select for our initial study something common, such as air, fire, earth, or water. Or, we might select on the basis of simplicity rather than on availability. However, to know what is simple is a very difficult and sophisticated task; one usually doesn't know until one understands the subject. From the vantage point of modern science certain of the chemical elements might be good choices for a simple substance. Neon has very simple physical properties, and krypton and xenon are relatively simple. In pure hydrogen the fact that the atoms always occur in pairs introduces a complication. Helium, while it might be expected to be simple, has surprised everyone by having properties when a liquid that are anything but simple.

For our purposes it is preferable to select substances which are suitable for experiments under conditions which can easily be obtained in the laboratory. We would prefer to work with pure, or at least, homogeneous substances and certainly we want to avoid toxic or otherwise dangerous materials. These requirements encourage us to begin our studies with common materials rather than simple ones. For this purpose the list of elements on which the Greeks based their science of matter is as good a place to start as any. Although our treatment of the knowledge will be different, we will share with the Greeks an interest, at times a fascination, with the simple substances of everyday life. However, we shall exclude fire from our list of common substances because after many centuries of experiments, we now know that fire is a condition rather than a substance. Many substances can attain this condition, substances whose other properties are very different, one from another.

Neither shall we examine the common substance earth in our initial experiments. A brief examination of some of the varieties of rock, sand, and dirt convince us that, though common, earth is very complex and is likely to be exceedingly hard to characterize with a few simple concepts. Earth is too far from simple to be attractive to beginning scientists.

Finally, then, we are left with the elements air and water. Both are common, both are relatively simple. At least, their properties seem to be uniform from place to place and from sample to sample. This uniformity is appealing. Perhaps if we could develop a disciplined, quantitative description of air and water, it would unlock the secrets of a much larger class of stuff. Of course, by water we mean here ice and steam as well. Water seems especially promising since it appears commonly as a gas (steam), as a liquid, and as a solid (ice). Our initial experiments will examine the properties of water in detail.

We begin our study by developing briefly the concepts of pressure and temperature. Historically, knowledge of the properties of matter and of the significance of pressure and temperature grew in parallel, each adding to the understanding of the other.

1.1 PRESSURE

We all know from our daily experience that solids and liquids have weight, that they fall to earth unless they are supported. Gaseous substances also have weight, about a thousand times less for the same volumes, but measurable nevertheless. It was only a few hundred years ago that this fact was established by the experiments of Torricelli, Pascal, and others. In order to support a body which has weight, an upward force must be provided equal to the magnitude of the weight. However, in addition to the magnitude of the force, its distribution over the body also may be important. Most of us are familiar with the effect of supporting a large weight

on a small surface area, for example, underneath a lady's sharp heel. A thumbtack is another example, in which a force applied to the relatively large area of the head is transmitted as an equal force applied by the very small area of the point. The point of the thumbtack and the lady's heel are able to penetrate into dense bodies, to produce deformations and compressions. Their effect, in fact, is dependent upon the ratio of the force to the area: the smaller the area over which a fixed applied force acts, the larger its effect; the bigger the area, the smaller its effect. The quantity called pressure was invented to represent this effect. It is computed by dividing the force by the perpendicular area over which it acts. Force is a vector quantity; it has magnitude and direction. However, we will postpone the question of whether or not pressure is a vector quantity. The numerical value of the pressure is expressed in units of weight (or force) divided by area. Common units of pressure are pounds per square inch (psi), newtons per square meter, and dynes per square centimeter.[3]

In the first experiments we will study pressure within a liquid, since it is usually easier to make measurements within liquids than within solids.

Experiment Sequence 1

From Experiment 1 we see that pressure is a property of the substance that can be measured and assigned a number at every point in the substance. At any point the value of the pressure does not depend upon the orientation of the surface on which it acts, and so we must conclude that the pressure is a scalar, not a vector, quantity, since it has a magnitude but no direction. When a real surface is introduced onto a liquid, the pressure against that surface results in a force perpendicular to the surface. It is the orientation of the area on which the pressure acts that determines the direction of the resulting force.

The pressure at a point within a liquid is ordinarily due to one or both of two factors. First, the weight of liquid above the point at which the pressure is observed contributes an amount equal to $w \times h$ where w is the weight per unit volume of the liquid, and h is the height to the free surface above the observation point. It is this pressure in the liquid that is supporting the liquid above. Second, if the surface of the liquid is not free but is confined by the container, any pressure exerted by the confining walls will be experienced unchanged throughout the liquid. The total pressure at any point in the liquid is the sum of the two effects, the confining pressure at the top of the liquid plus the "depth" pressure, $h \times w$.

Because of the depth effect, pressure is often expressed as the height of a column of liquid that the pressure under consideration could support, for instance in "feet of water" or "inches of mercury." This is a convenient shorthand. Since $P = h \times w$, giving h and the name of the liquid fixes the pressure completely. For example, to convert a pressure of "10 feet of water" to regular units we need to know the density of water, 62.4 pounds per cubic foot. Then P = "10 feet of water" = $h \times w$ = (10 feet)(62.4 lbs/ft^3) = 624 lbs/ft^2.

Pressure is more often reported in pounds per square inch than in pounds per square foot. We will change from one set of units to the other to illustrate a general method for converting units. We want to have $(inches)^2$ where we now have

[3] A newton is approximately the weight (force) of a bottle of ink, about 100 grams. A dyne is 1/100,000 of a newton or approximately the weight of a fly. A pound is about $4\frac{1}{2}$ newtons.

(feet)^2. Since 1 ft = 12 in., we may write

$$1 = \frac{12 \text{ in.}}{1 \text{ ft}} = \frac{1 \text{ ft}}{12 \text{ in.}}$$

and, of course, we may multiply by one as we wish. In this case we want (inches)^2 in the denominator so we multiply by one in the form (1 ft/12 in.)^2 and cancel units like algebraic quantities, where we can. Thus

$$P = 63.4 \frac{\text{lbs}}{\text{ft}^2} \times 1 = 62.4 \frac{\text{lbs}}{\text{ft}^2} \left(\frac{1 \text{ ft}}{12 \text{ in.}}\right)^2$$

$$= \frac{62.4}{144} \frac{\text{lbs}}{\text{in.}^2} = 4.35 \frac{\text{lbs}}{\text{in.}^2}.$$

In Experiment 1 we used a bicycle tire pump to vary the pressure in our apparatus. Yet the air pressure did not appear to exhibit the w × h variation that was observed with water and the other liquids. Either air behaves in quite a different way or its weight per unit volume is not large enough to produce observable effects in our experiments. Historically, the properties of fluid pressure (called hydrostatic properties) were well known more than a thousand years before the properties of air pressure were understood; as early as 400 B.C., Archimedes discovered the principle of hydrostatic pressure when he investigated the buoyancy of objects in water.[4] Much later, in the sixteenth century, Simon Stevin organized the hydrostatic laws into a unified whole much as we know them today.

In order to investigate the pressure properties of air, it is convenient to work with pressures below atmospheric pressure. There are several simple ways of doing this as we shall see in Experiment 2.

[4]The difference in the pressures on the bottom and the top of a body immersed in a liquid results in a net upward or buoyant force.

Experiment Sequence 2

In the course of your experiments on air, you have worked with a partial vacuum. The difficulty in removing the last bits of air from an apparatus made the "high vacuum" a subject more for discussion than for experimentation up until the seventeenth century. It has been known for a long time that a suction pump will not lift water more than 34 feet. Yet even Galileo did not recognize the principle behind this observation. He suggested, in fact, in an architectural engineering treatise on the strength of materials, that a solid column might break of its own weight at 34 feet. But his student, Evangelista Torricelli, attacked the question experimentally. He constructed a column of mercury which is nearly fourteen times heavier than water and found that the column when supported by the vacuum was only about one-fourteenth of the height of a similar water column. Torricelli's "vacuum gauge" was small enough to be a convenient laboratory tool. It was quickly put to use as a barometer when it was observed that the height of its column was a sensitive indicator of changes in the weather. Torricelli, however, was more interested in the vacuum in the space above the mercury, and he correctly reasoned that it was the pressure of the outside air that was supporting the mercury column. "We live . . . at the bottom of an ocean of air . . .," he said.

Torricelli's experiments were soon repeated and extended by others. Otto von Guericke of Magdeburg had two brass hemispheres constructed so carefully that when they were fitted together the air could be pumped out. The total force of the atmospheric pressure held them tightly together against the pull of two mule teams. Blaise Pascal commissioned the now famous experiment in which his brother-in-law Francois Perier carried a barometer from the base of a mountain

to the top and observed that the height of the column was ten percent smaller at the top, showing that there was a measurable change of atmospheric pressure with altitude.

The establishment of the existence of vacuum raised as many questions as it answered. The fluid air has properties quite different from those of water or other dense liquid substances. How is it that when a quantity of air is removed from a container, the remaining quantity expands to fill the void? And this ability to fill the void continues as long as any evidence of air remains. Robert Boyle attacked these questions with thousands of experiments, each carefully performed and faithfully recorded. It was his purpose to establish on a solid experimental base that matter is composed of particles: discrete little entities obeying the same mechanical laws as the planets and other material bodies. The thoughtful student may enjoy speculating, as did scholars of the seventeenth century, how a gas can be anything but tiny particles and still exhibit the behavior that we observe.

Let us now reconsider the pressure readings of our earlier experiments. Evidently the top surfaces of our liquids were not free at all, but were subjected to the nearly 15 pounds per square inch of pressure from the ocean of air in which we live. The indicated pressures, "gauge" pressures, represent increments above this atmospheric pressure. The true pressure at a point in a liquid or solid referenced against the vacuum is called "absolute" pressure. The difference between gauge pressure and absolute pressure depends on the elevation at which the measurement is made. It is usually more convenient to arrange an instrument to measure guage pressure than absolute pressure. In the latter case, the instrument must carry its own sample of the vacuum for reference.

We turn now to Boyle's experiments and examine carefully the "springiness of the air."

Experiment Sequence 3

Our experiences with liquids and gases indicate that gases are much more compressible than liquids. The expression for the dependence of volume on pressure (that is, volume as a function of pressure or V(P)) for most substances is complex. Gases which obey Boyle's law, PV a constant for fixed temperature, are a fortunate exception. For other substances we consider the dependence of V or P in terms of small changes in V, "ΔV"[5] caused by small changes in P, "ΔP", and use these quantities to give a quantitative meaning to "compressibility." We define the compressibility at constant temperature, the "isothermal compressibility" K, as the ratio of the fractional change in volume to the change in pressure causing it (or the fractional change in volume per unit change in pressure).

$$\frac{\Delta V}{V}\,\Delta P = -K$$

The negative sign is put in explicitly since volume decreases when pressure increases, so that K will be positive. This expression is frequently written

$$\frac{\Delta V}{V} = -\,K\Delta P,$$

and is sometimes also written

$$\frac{1}{K} = B = -\,\frac{V\Delta P}{V},$$

and B is called the <u>isothermal bulk modulus</u>. As we shall see, K (and therefore B) are functions of temperature and pressure, but they are slowly changing functions and frequently can be treated as constant.

[5]The symbol Δ is not a multiplier in the usual sense but is a mathematical operator. We shall read ΔV "delta vee" and understand it to mean a "small change in V." When ΔV is positive, the change produces an increase in V; when ΔV is negative, it produces a decrease in V.

The pressure and volume of a substance depend upon its temperature. We turn now to an examination of the concept of temperature so that we can examine this dependence.

1.2 TEMPERATURE

Temperature is the property of "stuff" which makes it sensibly hot or cold. In our common experience our bodies detect the temperature of a substance by touching it, by touching air which has touched it or by receiving radiation (heat or light) from it. Of the three methods of sensing temperature, actual contact is the most common and usually the most trusted. We learn to compare temperatures to the temperature of the human body which, fortunately, has a nearly fixed temperature. The temperature of the body stays the same not only from moment to moment but also from person to person. The near invariance of "body temperature" is probably the basis of most of our intuitive ideas about the concept of temperature.

It is well known that most materials expand when heated, that is, when they are raised in temperature. There are many exceptions to this behavior however. How can we proceed to attach a quantitative measure to our concept of temperature? What numerical values can we use, and how? We begin by searching for other fixed temperatures, similar to body temperature. There are many to choose from but one property of matter is common enough and invariant enough to be well suited to our purpose. At atmospheric pressure (14.7 pounds per square inch), water freezes and melts at a fixed temperature. That is, adding a water and ice mixture to a water and ice mixture produces no observable change in the temperature. The mercury column in a thermometer placed in the solution does not expand or contract as the mixing occurs. A finger placed in the mixture does not sense any temperature change. And this constant temperature condition holds until the mixture is either all ice or all water. After the ice is all melted or the water is all frozen a detectable temperature change may occur. In a later volume of this set the invariance of the temperature of the water-ice mixture is shown to be a property of a collection of a large number of microscopic things acting at random. The temperature of the water-ice mixture may vary but the variations are simply too small to detect.

A second fixed point can be obtained by observing that the temperature of boiling water does not change as the water is gradually converted into invisible steam. We can easily demonstrate this property with a thermometer or by mixing two pans of boiling water and observing the temperature of the combination (in this case, the use of a finger for a thermometer is not recommended!) The temperature at which the water boils is sensitive to the pressure of the atmosphere, however, so the fixed point must be defined for a given pressure, say for 14.7 pounds per square inch.

In 1724 Fahrenheit attempted to define a fixed temperature by adding salt to an ice and water mixture and defining the lowest temperature that could be reached in this way as "zero degrees of temperature." He chose body temperature as a second fixed point and called it "100 degrees of temperature." On modern-day Fahrenheit thermometers the boiling point is called 212°F and the freezing point 32°F. This makes the average body temperature 98.6°F and the coldest freezing point for an ice-salt-water mixture −6.4°F. All that remains of Fahrenheit's thermometer scale is his name! The use of the Fahrenheit scale lingers on in daily life in the United States and England where most people are familiar with weather data, recipes for cooking, and medical information in terms of Fahrenheit degrees.

We shall adopt the freezing and boiling points of water at atmospheric pressure as our fixed temperature

points and call them 0° and 100° Celsius,[6] respectively. Such a temperature scale is also frequently called "centigrade" because it has 100 graduations but such a nomenclature is misleading since Fahrenheit's scale also had 100 graduations. We shall write these temperatures 0°C and 100°C.

How can we proceed to determine temperature points intermediate between these two? We must continue to search out properties of matter which will let us define new fixed points. In Experiment 3 we used the mercury in the thermometer as a reference scale for comparing temperatures. For the time being, however, let us not put much faith in the absolute calibration of that mercury column.

Experiment Sequences 4, 5

Our experiments have shown us the difficulty of defining the intermediate points on a temperature scale. The properties of typical materials are not necessarily a linear function of temperature. Even the expansion of the mercury column itself may not be the same over the 0°C to 50°C part of the scale as it is over the 50°C to 100°C part. Thus, we can <u>define</u> the intermediate points of the scale most simply by assuming that some property of some substance is a linear function of its temperature. For instance, we could assert that when a heated mercury column expands the fractional expansion is the same for equal temperature increments. In symbols we would write this as

$$\frac{\Delta V}{V} = \beta \Delta T \qquad (1.1)$$

where β is a constant called the isobaric[7] coefficient of thermal expansion, and we assume that the pressure has been held constant. To tie the fundamental scale of temperature to the behavior of a single metal would not give us much confidence in the utility of the concept for describing all material substances. Let us perform some experiments similar to those of Experiment 5, this time using gases as our test materials. We shall find that most gases behave similarly with temperature.

Experiment Sequence 6

Our experiments with gases have shown that they may be used to define a temperature scale much more reliably than can liquids or solids. So long as the gas is not near its condensation point, the change in volume seems to be proportional to its temperature.

The volume versus temperature data obtained from Experiment 6 can be plotted as a family of straight lines. We express this fact mathematically by writing

$$V = A + CT, \qquad (1.2)$$

where A and C are constants. The number A is equal to the numerical value of the volume when T = 0°C on the mercury thermometer. The number C is the slope of the curve. When the ratio A/C is computed for the various gases of our experiments we find that its value does not change from one gas to another, nor from one experiment on a given quantity of gas to another experiment using a larger or smaller quantity. Precise measurements give the value of A/C to be +273.16°C[8]. A typical gas

[6] In 1742 Anders Celsius, a Swedish astronomer, reported constructing a mercury thermometer which he placed in the snow for one half hour, marking the height of the column. Then he put the thermometer into a teapot of boiling water and after marking the height he divided the interval between the marks into 100 equal parts. All this was done at the median barometric pressure. However, he marked the upper point 0 degrees and the lower one 100 degrees!

[7] Constant pressure.

[8] Notice that the units of A are those of a volume (cm^3, liters, in^3, etc.), while those of C are volume per unit temperature. Therefore A/C has the dimensions of a temperature.

might then be expected to vanish altogether ($V \rightarrow o$) if the temperature were to go as low as $-273.16^{\circ}C$. The actual possibility of this is intriguing. The very low temperatures involved require more sophisticated apparatus than is available to us, but attempts to reach such very low temperatures have been made by many nineteenth- and twentieth-century scientists. Unfortunately, any gas chosen begins to condense at temperatures far above $-273^{\circ}C$. The most nearly successful attempts are made with helium which does not become liquid until it is cooled to $-268.9^{\circ}C$. Later, in the study of thermodynamics, we will find that there are good reasons to believe that the limiting temperature of $-273^{\circ}C$ can only be approached, but cannot be achieved by natural systems.

The existence, at least the hypothetical existence, of a single invariant temperature for all gases suggests that we might choose that temperature as a fixed point for a new temperature scale, calling this lowest point "0° absolute" or as is now more common, "0° Kelvin" after the English scientist who worked diligently to solve many problems in the theory of heat. The temperature intervals are chosen identically with the Celsius intervals so that the freezing point of water is $+273.1^{\circ}K$ and the boiling point is $+373.1^{\circ}K$. The freezing-point to boiling-point interval is still exactly 100 Kelvin degrees, or $100K^{\circ}$. The Kelvin scale is in widespread use only by scientists. We shall in these pages report temperatures and temperature intervals in $^{\circ}K$ and K° when the use of these units will emphasize the physical importance of the Kelvin temperature scale.

It often happens in physics that a property will be carefully defined using observations of one phenomenon, and then will be measured using instruments of an entirely different kind. For example, although we define pressure in terms of force per unit area we measured it with a calibrated gauge whose pointer rotates over a dial. When measuring temperature a similar process is followed. The temperature is defined in terms of the expansion of a gas. The behavior of a large number of gases is sufficiently similar to permit this definition. In practice, however, it is much more convenient to use a calibrated mercury thermometer to measure temperature since it is small, rugged, and cheap. We shall assume that the thermometer has been carefully calibrated by comparing it to a gas thermometer.

Many other kinds of thermometers are possible. The list of physical properties of matter which depend on the temperature is seemingly endless and any such property can be used as a thermometer if it is suitably calibrated. The most common properties used for this purpose are electrical: the voltage of a chemical cell, for example, or the voltage which is established at the contact between two dissimilar metals. Electrical voltages can be measured so precisely and conveniently that thermometers using the junction potential between metals are very common. Such devices are called thermocouples. When two dissimilar metals are arranged in a loop to form an electrical circuit, two junctions must be made. The potential, and therefore the current which flows, depends upon the temperature difference between the junctions. Since the voltage is not a linear function of the temperature, a careful calibration of the thermocouple against a gas thermometer or other standard is necessary. Other electrical properties which are sensitive to changes in temperature are also used as thermometers. The change in electrical resistence with temperature is very commonly used.

In the course of the temperature experiments several important properties of heat and temperature were observed which should be stated formally. For example, we note that two bodies which are at the same temperature do not change temperature when brought into contact. If they exhange heat, the same amount of heat goes from A

to B as goes from B to A, since neither body shows a change in heat content. They might both warm up or both cool down because of contact with their surroundings, but then the surroundings constitute a third body. Our statement does not include the effect of a third body. It is on this observation that the concept of "thermal equilibrium" is based. Bodies are in thermal equilibrium when they are at the same temperature.

A second part of the definition of temperature is that heat always flows from the hotter to the cooler of a pair of bodies. That is, the bodies tend to approach equilibrium. This principle may equally well be regarded as the definition of hot compared to cold. We shall have more to say about heat, its transfer among substances, and its relation to energy.

1.3 SUMMARY

Although the experiments we have performed were intended to illuminate some basic physical concepts, namely, the concept of pressure and temperature, some basic physical properties of matter itself have also been revealed. We have experimented with the three common forms of matter - gases, liquids, and solids - and have found them to differ widely in density and compressibility. We have found that matter usually expands when it is heated and that it contracts when it is squeezed. When many substances change their state, say from gas to liquid, or liquid to solid, or gas to solid, they do so at constant temperature. That this is not a universal result is evident from the behavior of molten glass or warm butter, but it is a sufficiently widespread property to be noted here. Later we shall find it convenient to describe the states of matter as gaseous, liquid, amorphous, and crystalline. When a substance melts, crystallizes, boils, or condenses the temperature at which this occurs <u>is</u> constant.

We have obtained a considerable amount of data on gases and reduced much of it to simple algebraic expressions. We can combine the results of the pressure-volume experiments and of the volume-temperature experiments into the single formula,

$$PV = \text{const } T, \qquad (1.3)$$

with the understanding that T is to be measured in degrees Kelvin. The next experiment will examine this assertion in more detail.

Experiment Sequence 7

This expression, a relation between P, V, and T, is called the equation of state of the gas. It is a good description of the behavior of most gases at temperatures far from their boiling (or condensation) points. For lower temperatures the pressure will generally be less than that predicted by the formula. The constant which appears in the equation of state of a gas clearly must depend on the amount of gas being described, that is, its mass or weight. We might write a new expression,

$$PV = \text{const } MT, \qquad (1.4)$$

to make this explicit, or we might write, dividing through by the volume,

$$P = \text{const } \frac{M}{V}T = \text{const } \rho T, \qquad (1.5)$$

where ρ is the mass-per-unit volume or the density of the material.[9]

[9]The student who has studied elementary chemistry will be interested in a further consideration of the constant which appears in Eq. (1.5). The equation of state of an ideal gas can be written.

$$P = \frac{R}{M_0}\,\rho T.$$

R is a universal number, called the gas constant. When the density is expressed in Kg/m^3, the pressure in newtons/m^2 and M_0 in grams, the value of R is 8335. M_0 is the gram molecular weight of the gas. It is the weight, expressed in grams, of 6×10^{23} molecules.

Most of our study of the behavior of matter will resolve itself into attempts to describe the equation of state of different materials. Because the possible states, such as solid and liquid, are so different in their behavior it is extremely difficult to write a single equation of state in a simple form for any substance. It is unlikely that there is an expression that would describe <u>all</u> substances universally. Yet there are patterns of behavior which are common to all substances and our following experiments and discussion will describe some of these.

2 EQUATIONS OF STATE

2.1 GASES

We saw in Chapter 1 that many gases could be described approximately by the simple equation of state

$$PV = \text{const } T. \qquad (2.1)$$

Gases which are exactly described by Eq. (2.1) are called ideal gases. For real gases the range of validity of this expression is limited by the condensation point, where the gas begins to become a liquid; however, it is usually when the density of the gas is large that deviations from the ideal behavior occur. The density of a gas can be increased either by lowering its temperature or by raising the pressure. Most common gases behave ideally at pressures below two atmospheres. The next experiment sequence is intended to reveal variation from ideal gas behavior for some common gases.

Experiment Sequence 8

At high pressures the volume occupied by a real gas is smaller than would be the case for an ideal gas. A useful way to represent this behavior is by the so-called "virial expansion." The virial expansion is a correction to the ideal gas equation of state obtained by adding on additional terms. We choose to express these corrections as polynomial functions of the temperature and pressure. The successive correction terms are then $A(T)P$, $B(T)P^2$, $C(T)P^3$, etc. So long as the temperature dependent terms $A(T)$, $B(T)$, . . . , are sufficiently small the corrections can be each enough smaller than the preceding to guarantee that the series approaches an exact value after a few terms. Thus, the viral expansion lets us write the equation of state in the form

$$PV = A(T) + B(T)P + C(T)P^2 + \ldots . \qquad (2.2)$$

The functions $A(T)$, $B(T)$, etc., are called the coefficients of the virial expansion in pressure, and depend on the mass of gas in the system, the kind of gas, and the temperature. We can use the data obtained in Experiment 8 to compute some of the virial coefficients for those common gases. When one knows all the virial coefficients for a gas, he has, in effect, a complete description of the gas in terms of P, V, and T. For an ideal gas, $B(T) = C(T) = \ldots = 0$, and $A(T) = R\,T$. As a gas departs from ideal behavior, the higher order coefficients $B(T)$, $C(T)$, etc., become larger. As the gas approaches the liquefaction point, the high order [$D(T)$, $E(T)$, etc.] coefficients become sufficiently large that the series must include more and more terms until finally an infinite number of terms is required in order to describe the substance accurately. In other words, the virial expansion is not useful for describing gases near the boiling point.

A very large number of equations of state have been proposed over the years. Some of these involve many arbitrary constants or "fitting parameters" and some only a few. All are attempts to describe accurately in mathematical symbols the observed behavior of real gases. When one attempts to fit algebraic formulas to the data over a wide range of pressures and temperatures, including the condensation region, the resulting expression is usually complicated and tedious to use. One very simple ex-

$PV = \text{const } T(1 + BP + CP^2 + DP^3 + \ldots)$ with pressures expressed in atmospheres.

	T = 200°K	300°K	400°K
ARGON	$B(T) = -2.941 \times 10^{-3}$	-6.31×10^{-4}	-2.6×10^{-5}
	$C(T) = -3.91 \times 10^{-6}$	1.2×10^{-6}	8.1×10^{-7}
	$D(T) = 28.47 \times 10^{-9}$	11.6×10^{-9}	4.2×10^{-10}
NITROGEN	$B(T) = -2.125 \times 10^{-3}$	-1.83×10^{-4}	2.79×10^{-4}
	$C(T) = -8.01 \times 10^{-8}$	2.08×10^{-6}	1.14×10^{-6}
	$D(T) = 5.727 \times 10^{-8}$	2.98×10^{-9}	-9.7×10^{-10}
OXYGEN	$B(T) = -2.98 \times 10^{-3}$	-6.051×10^{-4}	1.19×10^{-5}
	$C(T) = -6.60 \times 10^{-6}$	6.0×10^{-7}	7.2×10^{-7}
	$D(T) = 5.15 \times 10^{-8}$	8.65×10^{-9}	-5.14×10^{-10}

Table 2.1 Virial coefficients for several common gases.

pression for the equation of state of real gases was proposed by the Dutch physicist, van der Waals:

$$(P + a/V^2)(V - b) = RT. \qquad (2.3)$$

Only two arbitrary constants (a, b) occur and the agreement with experiment is excellent for a large class of substances. The van der Waals equation of state holds fairly well even into the liquid region of the substance. Some of the virial coefficients and the van der Waals coefficients of a few common gases are listed in Tables 2.1 and 2.2.

$(P + a/V^2)(V - b) = RT$, with pressures expressed in atmospheres and volume in liters.

	a	b
Ne	.0211	.0171
Ar	1.345	.0322
N_2	1.390	.0394
O_2	1.360	.0318
CO_2	3.592	.0427

Table 2.2 Van der Waals constants for several common gases.

2.2 LIQUIDS

Liquids and solids are, as a rule, much more dense and much less compressible than gases. Extremely large pressures are necessary in order to produce appreciable compression of these materials. In Experiment 9 we shall examine the change in volume of a few selected materials as a function of pressure for several fixed temperatures.

Experiment Sequence 9

We learned earlier to express the compressibility of materials in the simple form

$$\frac{\Delta V}{V} = K\Delta P. \qquad (2.4)$$

An expression which is more suitable for the description of a liquid is that due to Tait:

$$\Delta V = -\frac{K\Delta P}{L(T) + P}, \qquad (2.5)$$

where L is a function of temperature. In equations like (2.4) and (2.5), a

small change in volume, ΔV, is related to a small change in pressure, ΔP. Such an equation is called a differential equation. Differential equations are usually less convenient to work with than ordinary algebraic relations. A differential equation is "solved" when it is replaced by an equivalent algebraic equation. We shall illustrate below an example of one method of solving a differential equation by finding a suitable functional relationship for V(P) which can replace Eq. (2.5).

If we let $p \equiv L + P$, then a pressure change, ΔP, results in an equal change, Δp, in the new variable p, which we shall call the reduced pressure. Thus, since $\Delta P = \Delta p$,

$$\Delta V = -\frac{K\Delta P}{L + P} = -\frac{K\Delta p}{p}, \qquad (2.6)$$

making the equation simpler.

The function $V = -K \ln p$ is a function which has the property we want. That is, if

$$V = -K \ln p, \qquad (2.7)$$

then

$$\Delta V = V_1 - V_2 = -K \ln p_1 + K \ln p_2 \qquad (2.8a)$$

$$= -K(\ln p_1 - \ln p_2) \qquad (2.8b)$$

$$= -K \ln p_1/p_2 . \qquad (2.8c)$$

Since $\Delta p = p_1 - p_2$, then $p_1 = p_2 + \Delta p$ and

$$\Delta V = -K \ln\left(\frac{p_2 + \Delta p}{p_2}\right) \qquad (2.8d)$$

$$= -K \ln \left(1 + \frac{\Delta p}{p_2}\right). \qquad (2.8e)$$

This form is not yet what we were looking for, but its approximation for small Δp is Eq. (2.5). The logarithm function crosses the abscissa at 45° at $(\Delta p/p) = 1$ (see Fig. 2.1), so that $\ln(1 + \Delta p/p_2) = \Delta p/p_2$, when $\Delta p/p_2$ is small. Using this fact and writing p for p_2, we have

$$y = \ln\frac{(\Delta p)}{p}$$

$$\Delta V = -\frac{K\Delta p}{p} = -\frac{K\Delta p}{L + p}. \qquad (2.9)$$

The function $V = -K \ln (L + P)$ satisfies the Tait differential equation. We can repeat the steps above to show that all of the functions,

$$V = A - K \ln [L(T) + P], \qquad (2.10)$$

are also solutions as the constant A takes on all possible values. Except at very high pressures, the Tait equation describes the experimentally observed properties of a large number of liquids very closely. The constant A and the function L(T) which expresses the temperature dependence must be determined for each liquid.

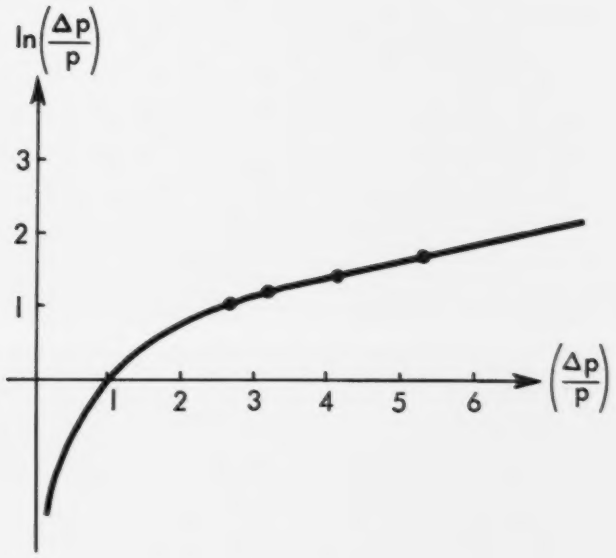


Fig. 2.1

Experiment Sequence 10

2.3 SOLIDS

Solid bodies can be separated into two large classes, those that have

fixed melting temperatures and those that do not. A closer inspection of the solids whose melting temperatures are fixed reveals that their atomic structure is regular; these solids are called crystalline. Many crystals will show a regular geometric surface with planar faces, and the angles between the planes have definite values characteristic of each material. When the crystal is broken up into fragments, geometric features are retained in the fragment particles. The surfaces are, as before, planes intersecting at fixed and well-defined angles. The atomic structure of crystals influences (in addition to the external shape of the crystals) the electrical and magnetic properties, the heat conduction, strength, elasticity, and other properties.

It is useful to think of a crystalline material as if it were composed of a very large number of identical prisms fitting tightly together with no voids and all oriented alike. The observed geometric properties of the crystal can be represented in this model. In an actual crystal the smallest repeating unit, or "unit cell" as it is called, may include only a few atoms and be as little as 5×10^{-8} cm. on an edge.

There are seven types of prisms which can be assembled into crystal-like structures, and each type can be given a name descriptive of its symmetry. Thus, we have cubic, tetragonal, trigonal, rhombohedral, hexagonal, monoclinic, and triclinic forms. A crystal whose symmetry is cubic will show the same compressive behavior in one direction as any other, while a hexagonal crystal can be expected to deform differently in the direction of the symmetry axis than at right angles to it. When the physical properties of a substance are independent of the direction in the material along which they are measured we say the substance is isotropic; when the property depends upon direction in the material, we say the substance is anisotropic.

Experiment Sequence 11

Many solid materials are polycrystalline: composed of very small crystals collected together into the large body with random orientation. The properties of these substances generally appear isotropic due to the effect of averaging over the random orientation of all the crystallites. The melting points of such solid aggregates are usually just as con-

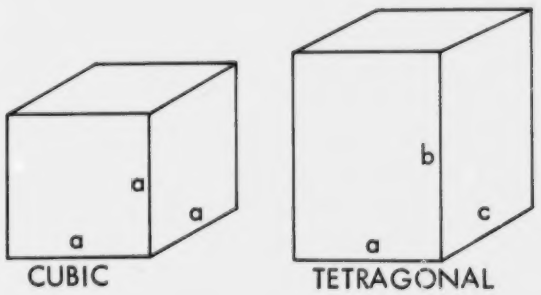


Fig. 2.2

stant as those of single crystals, indicating that the laws of melting are determined on a microscopic scale.

When a solid body, crystalline or not, is deformed along a single direction, the description of the behavior is usually represented in a form similar to that for the volume change with pressure. We write

$$\frac{\Delta \ell}{\ell} = - \text{ const } \Delta P \qquad (2.11)$$

where ℓ is the original length of the body. If we rewrite Eq. (2.11),

$$\Delta P = - \text{ const } \frac{\Delta \ell}{\ell}, \qquad (2.12)$$

the constant which appears is called "Young's Modulus," Y, or the modulus of elasticity for the material. If the material is anisotropic, the modulus will be a function of the direction in the material in which the compression or elongation occurs. The modulus will also be a function of temperature. Table 2.3 lists the moduli of elasticity for a number of common materials.

A simple relationship exists between the modulus of elasticity and the bulk modulus of the material. Imagine a cube of solid material of side ℓ subjected to an over-all pressure increase ΔP. Each edge of the cube will decrease by an amount $\Delta \ell$ where the magnitude of $\Delta \ell$ is given by

$$|\Delta \ell| = \frac{\ell \Delta P}{Y}. \qquad (2.13)$$

The total volume of the block will now be $(\ell - \Delta \ell)^3$ and the change in volume of the block will be

$$\Delta V = \ell^3 - (\ell - |\Delta \ell|)^3 \qquad (2.14a)$$

$$= \ell^3 - (\ell^3 - 3\ell^2 \, |\Delta \ell| + 3\ell \, |\Delta \ell|^2 - |\Delta \ell|^3) \qquad (2.14b)$$

$$= -3\ell^2 \, |\Delta \ell| + \text{small terms}. \qquad (2.14c)$$

Since $\Delta \ell$ is small compared to ℓ we may discard the small terms in $\Delta \ell^2$ and $\Delta \ell^3$ and write

$$\frac{\Delta V}{V} = - \frac{3\ell^2 |\Delta \ell|}{\ell^3} = - \frac{3|\Delta \ell|}{\ell} \qquad (2.15a)$$

$$= - \frac{3\Delta P}{Y}. \qquad (2.15b)$$

From (2.4b), solving for Y, we have

$$Y = - \frac{3V\Delta P}{\Delta V}. \qquad (2.16)$$

This expression can be compared to the definition of the bulk modulus

$$B = - \frac{V\Delta P}{\Delta V}, \qquad (2.17)$$

from which we see that

	dyne/cm^2	newt/m^2	lbs/in^2
IRON (PURE)	2.37×10^{11}	2.37×10^{10}	3.41×10^{6}
COMMERCIAL	10 to 20 $\times 10^{11}$	10 to 20 $\times 10^{10}$	14.4 to 28.8 $\times 10^{6}$
DIAMOND	10.76×10^{11}	10.76×10^{10}	15.5×10^{6}
NaCl (SALT)	0.486×10^{11}	0.486×10^{10}	0.699×10^{6}
QUARTZ	5.9×10^{11}	5.9×10^{10}	8.5×10^{6}
ALUMINUM	1.08×10^{11}	1.08×10^{10}	1.556×10^{6}
ROLLED	$\sim 7.0 \times 10^{11}$	$\sim 7.0 \times 10^{10}$	10.1×10^{6}
COPPER (PURE)	1.684×10^{11}	1.684×10^{10}	2.425×10^{6}
DRAWN OR ROLLED	$\sim 12.0 \times 10^{11}$	$\sim 12.0 \times 10^{10}$	17.29×10^{6}

Table 2.3 Modulus of elasticity.

$$Y = 3B. \qquad (2.18)$$

The preceding discussion ignores the fact that when a body is squeezed along a certain axis it tends to expand slightly perpendicular to that axis. The expansion is inhibited when the squeeze is applied to all parts of the body simultaneously, so a typical body appears to be slightly "stiffer" when squeezed in volume than when squeezed in one direction only. That is, in general,

$$Y < 3B. \qquad (2.19)$$

For more discussion about the elastic properties of solids, the student should read one of the standard works on solid state physics, such as the books by that title by Kittel and Becker.

If a solid body returns to its original shape and size when a deforming pressure is removed, it is said to be elastic. Nonelastic deformations result in a permanent change in the shape or size of the body. Almost all of the nonelastic deformations which we observe in crystalline materials are due to imperfections in the crystal, that is, to voids and foreign atoms which disturb the regular geometric arrangement. For example, in a highly stressed single crystal, missing particles may permit some migration of the material. In a highly stressed polycrystalline material, the crystallites also may move slightly past one another to relax the strain. The relaxation of a stressed solid takes place more quickly at higher temperatures.

Some solids do not show any crystalline properties whatever; for example, they do not have well-defined melting points. Yet they appear to be hard, elastic materials. Examples of such amorphous substances are glasses, waxes, and polymers or "plastics" of various kinds. Amorphous substances are almost always isotropic. Their physical properties are intermediate between crystalline solids and liquids. One can see an example of this in the old window panes to be found in Europe or New England. After many hundreds of years the glass has flowed down so that it is much thicker at the bottom than at the top. Probably it will keep flowing like a liquid until it is just a blob of glass if it is left undisturbed for long enough.

The physical properties of amorphous substances change much more rapidly with temperature than those of crystalline materials. This offers additional support to the idea that amorphous materials act like supercooled liquids.

The same material may occur sometimes as a crystalline solid and sometimes as an amorphous solid. For example, quartz may be crystalline or, if melted and cooled quickly, amorphous. There are other substances which are not well described as either crystalline or amorphous, such as the fibers of nylon or dacron. These fibers have quite different physical properties lengthwise than the properties they possess across the fiber at right angles. Similarly, glass may be prepared in fiber form and found to be much stronger and more elastic than in bulk.

Experiment Sequence 12

Experiment Sequence 13

3 H E A T

3.1 EARLY STUDIES OF HEAT

The nature of heat has been one of the most sought after and elusive concepts in physics. The list of scientists who have contributed to its understanding is impressive indeed: Bacon, Galileo, Boyle, Leibnitz, Hooke, Newton, and in more recent years, Joule, Maxwell, and Gibbs. It was Sir Isaac Newton himself who suggested that heat was the megascopic phenomenon which described the microscopic motions of tiny corpuscles. And yet this suggestion, which comes so close to the truth, was rejected because it failed to describe two essential phenomena: what is fire, that most dramatic evidence of heat, and how is heat able to traverse the vacuum, from which all corpuscles have been removed? For 150 years after Newton, natural philosophers proceeded to explore one blind alley after another before returning in the nineteenth century to what is essentially Newton's scheme.

The most satisfying models were those of Franklin and Boerhaave. It is not surprising that Benjamin Franklin should recognize an analogy between the flow of an electric charge, a subject in which he was very much interested, and the flow of heat. The temperature difference controls the flow of heat, much as the potential difference in an electrical circuit controls the flow of current. The words "flow" and "current" suggest something with the properties of a "ponderable" fluid. This fluid was given the name "phlogiston."

Experiment Sequence 14

In spite of the success of the fluid model of heat in describing the conductivity of heat through matter, it didn't deal with the central question, the nature of fire. The prevailing theory assumed that phlogiston flowed from the flame, pouring into any body with which it came in contact. But a true theory of heat must also explain chemical reactions. Lavoisier was probably the greatest chemist of all time; certainly he was the teacher of his entire generation. Lavoisier set himself the task of understanding fire, more particularly the burning of metals. His apparatus embodied some of the finest craftsmanship of France. Under a glass jar on a beam balance he carefully burned a small quantity of mercury and found that the system neither gained nor lost mass. Phlogiston, if it exists, has no weight. Yet the mercury oxide is heavier than the metal from which it is made. Lavoisier correctly deduced that the mercury had combined with some part of the air. Later, other experiments showed the process to be reversible; some air could be gotten from the mercury oxide. Further experiments extended the principle to other metals and then to other materials. The burning of a substance is a complicated process of combining matter, quite apart from the heat which is evolved or required in the reaction. Although it was the Englishman Joseph Priestley who isolated oxygen, the combining element of the air, Lavoisier gave it its name.[10] Later, learning from the work of Cavendish, he showed that the burning of hydrogen in air results in the single substance water, and from this he deduced the key to the whole of chemistry, the laws of combining weights. The notion of molecular formu-

[10] In fact, in collaboration with Guyton de Morveau, he invented the rules for naming chemical compounds and named many of the elements himself.

las and the molecules themselves followed quickly.

In his experiments with heat Lavoisier measured and catalogued a large number of heats of reaction, the heat liberated when substances combine chemically. He also measured some heat capacities, the heat needed to warm a body a given amount. From these latter results it was established that for each substance a very definite quantity of heat is required to produce a given temperature change, although the amount of heat required to take a body from 0°C to 10°C may be quite different from the amount of heat required to warm the same body from 90°C to 100°C.

Before repeating Lavoisier's experiments on heat with our own apparatus, we can benefit from an examination of one additional set of heat experiments. Benjamin Thompson was an American colonist, scientist, and adventurer who returned to Europe in disgust at the success of the American revolution. He assumed a position as Minister of War of Bavaria, taking the title Count Rumford. Among his duties was supervision of the boring of cannons and Rumford quickly saw the connection between the work done in cutting the metal and the heat generated by the process. Careful experiments confirmed his ideas. A cannon kept at constant temperature by using water as a coolant would heat the water in proportion to the number of turns of the barrel against the cutting tool. If phlogiston were a real substance it would be possible to create an unlimited amount of it by continuing the boring process indefinitely. Instead it seemed a better interpretation that heat is just another manifestation of the energy or work which is put into turning the cannon in the lathe.[11]

[11]An irony of history: Lavoisier's wife, Marie Anne, had been his devoted assistant and secretary throughout that great man's scientific career. After his death at the hands of the French revolutionists, Marie Anne married Rumford and spent her last years in his company. It was not a happy union.

Experiment Sequence 15

Therefore, to measure heat energy we may either measure the warming effect or we may measure the work done in generating the heat. James Prescott Joule was the first to measure accurately the relation between the work done in producing heat and the temperature rise which results.

The standard unit of heat energy or "calorique" was assigned by Lavoisier who defined a "calorie" to be the heat required to warm a gram of water one Celsius degree.[12] The standard unit of work is named for Joule himself. One joule is the work done by a constant force of one newton acting through a distance of one meter. Since one newton is about the weight of a bottle of ink (100 grams), one joule is approximately equal to the kinetic energy of a bottle of ink which has fallen from rest through one meter. In terms of these units, Joule's experiments established that

1 calorie = 4.187 joules.

In this experiment and those which follow we shall need a quantitative and reproducible source of heat. For this purpose mechanical devices, or burning candles, or gas flames are not convenient; we shall instead assemble an electrical heater which converts electrical energy into heat energy at a fixed rate. The mechanical energy is originally converted into electrical energy at some remote point, presumably by the electric power company. The electrical circuit is then a convenient way to transport the energy to the laboratory where it can be con-

[12]Actually, the "small calorie" is that amount of heat required to raise one gram of water from 3.5°C to 4.5°C. The "normal calorie" is that amount of heat required to raise one gram of water from 14.5°C to 15.5°C. The "mean calorie" is 1/100th of the amount of heat required to raise one gram of water from 0°C to 100°C. The ordinary calorie familiar to dieters is the "large calorie" or "kilogram calorie." It is equal to 1000 small calories.

verted into heat. Such a heater is calibrated in terms of the number of joules of heat energy delivered per second, a unit called a "watt." We shall assume that our heater delivers a fixed number of watts regardless of the material in which it is immersed or the temperature of that material.

Experiment Sequence 16

3.2 HEAT CAPACITY

It was originally thought that the ability of a body to contain heat depended only on the mass of material available. Like many other intuitive ideas this one was abandoned when confronted with the facts derived from experiment. The first and simplest experiment involved two vessels placed near a fire, one containing water and the other an equal weight of mercury. The mercury was warmed much faster and then when the vessels were removed from the fire it also cooled much faster. Joseph Black, prompted by this observation, performed a careful experiment in which equal parts of hot mercury "at the 150th degree" and cold water "at the 100th degree" were mixed. The resulting mixture reached equilibrium at 120 degrees. When equal parts of hot water and cold water at these temperatures were mixed the final temperature was 125 degrees. From this, Black concluded that bodies vary in their ability to absorb heat.

We define the heat capacity of a body as the amount of heat necessary to change its temperature 1 degree. We will usually express the heat capacity in joules per Celsius degree. Careful experiments on water show a small change in its heat capacity as the temperature varies. It is agreed to select water at 4°C[13] as a standard material for the definition of the calorie and therefore the heat capacity. When the thermal properties of materials are compared, it is convenient to use the specific heat, defined to be the ratio of the heat capacity of the substance to the heat capacity of water at 4°C.

A substance with a large capacity might be imagined to have many types of internal motion, or fewer types with large amplitudes. It is clear from Experiments 16 and 17 that the temperature of a body is not enough to tell us what its internal energy is. Two bodies at the same temperature may differ widely in internal energy.

Experiment Sequence 17

Large changes occur in the heat capacities of solids at low temperatures. The removal of even a small amount of heat may result in a relatively large temperature drop, suggesting that internal motions are being "frozen out."

The heat capacities of ordinary liquids seldom show large changes. Gases vary widely in their heat capacity. The heat capacity of a gas with a complex molecular structure is generally higher than that for a simple monatomic or diatomic gas, suggesting again that the internal structure is playing a role.

Experiment Sequence 18

When a gas is heated in a closed container at constant pressure the gas expands. Some of the heat energy is used to drive back the confining piston or membrane. The balance of the heat energy causes the temperature of the gas to rise but the temperature necessarily goes up less for the same input of heat than it would in a gas which was held at a fixed volume. Thus, there are two heat capacities, one at

[13] The fact that the heat capacity differs from substance to substance and at different temperatures suggests that there is internal structure whose motion plays a role in the ability of the body to contain energy.

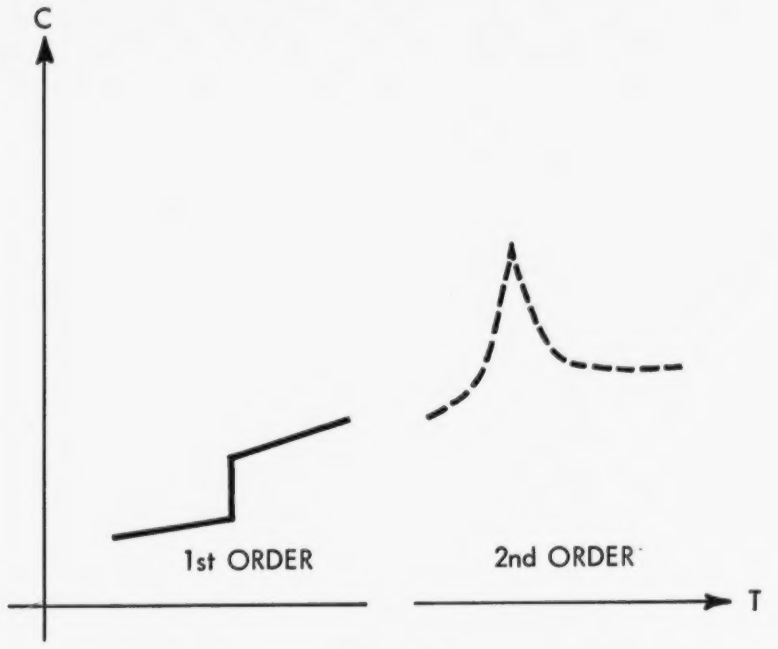


Fig. 3.1

fixed pressure and one at fixed volume. For gases these may differ by 25%, but for solids and liquids whose thermal expansion is much smaller the two values are nearly equal.

Experiment Sequence 19

Joseph Black was also interested in the melting and boiling of substances. It had been assumed that when a substance had been warmed to the melting point a small addition of heat was all that was necessary to convert it all to liquid. Black, using his method of mixtures, showed that a great deal of warm water was required to melt a small quantity of ice. He also showed that a great deal of heat is required to evaporate a liquid even compared to that required to raise its temperature from freezing to boiling.

Experiment Sequence 20

The heat which must go into or out of a substance to change its state is called the latent heat. The changes in the physical state of matter such as from gas to liquid, liquid to solid, gas to solid, which have latent heats associated with them are called first-order phase transitions. Frequently, crystalline solids will undergo changes in structure, for instance from hexagonal to cubic at particular temperatures. Such changes also show a latent heat. However, solids may also undergo changes which do not show latent heats. For example, a magnetic material when heated will become nonmagnetic at a definite temperature characteristic of the material, called the Curie temperature. Such a transition is called a second-order phase change.

In a first-order phase transition there is a discontinuity, a step, in the specific heat curve. In a second-order transition, there is a cusp in the specific heat curve as illustrated in Fig. 3.1.

4 PHASE AND PHASE DIAGRAMS

4.1 BOILING

We have investigated the freezing and boiling of several materials and noted that such transitions occur at a definite temperature and require a definite amount of heat for a definite amount of material. All of our experiments were performed at atmospheric pressure. We can expect a variation in both the temperature and the latent heat when the pressure is varied. In our initial experiments let us examine the boiling of a liquid as a function of pressure.

Experiment Sequence 21

When the pressure at which a liquid boils is plotted against the temperature, the points fall on a line which is called the vapor pressure curve. Each point represents a pressure and temperature condition at which both liquid and vapor can coexist in unlimited amounts and both must be present. This is a new kind of equilibrium, different from thermal equilibrium in which two substances can coexist at the same temperature at any pressure. The vapor pressure curve terminates at the high temperature end in what is called the critical point. At this temperature and pressure the density of the gas and of the liquid are identical. At higher temperatures there is no difference between gas and liquid. Because the distinction between gas and liquid vanishes at the critical point, the latent heat required to convert a liquid to a gas also must vanish there. Hence, the latent heat must be temperature dependent.

One property of the substance that illustrates the difference between gas and liquid is the scattering of light. When a very bright, well-collimated beam of light is passed through a gas and the gas is viewed at right angles to the beam, very little light is seen. In a liquid, however, the scattered light may be 1,000 times as intense. When a liquid is examined very near the critical point, the sudden change in light scattering is dramatic evidence of a change in the state of the material.

Experiment Sequence 22

The liquid vapor equilibrium curve terminates on the low end because the material freezes. But since the liquid and vapor coexist at each point of this curve, the low end of the curve must be a point at which liquid, vapor, and solid coexist, the triple point of the substance. The coordinates of the triple point of water are $T = .0099^\circ$ and $P = 4.57$ mm mercury.

The vapor pressure data obtained in Experiment Sequence 21 can be represented by functions of the form

$$P = A \ln T + B, \qquad (4.1)$$

where A and B are numbers characteristic of the substance. This relationship is approximately true for all vapor pressure curves, and suggests there may be an underlying meaning or principle which may have escaped our attention. One method of searching for such a principle is the method of dimensional analysis. Let us attempt to learn something about the numbers A and B by applying purely logical arguments. For one thing, A and B have the dimensions of pressure. We might ask, "Is there a characteristic pressure associated with each liquid?" Perhaps there is; for example, we

SUBSTANCE	PRESSURE					
	1mm	10mm	40mm	100mm	400mm	760mm
1 NITROGEN (N_2)	−226.1°	−219.1	−214.0	−209.7	−200.9	−195.8
2 OXYGEN (O_2)	−219.1°	−210.6	−209.1	−198.8	−188.8	−183.0
3 ACETONE (C_3H_6O)	−59.4°	−31.1	−9.4	7.7	39.5	56.5
4 METHANOL (CH_3OH)	−44.0°	−16.2	5.0	21.1	49.9	64.7
5 DIOXANE ($C_4H_8O_2$)	−35.8°	−1.2	25.2	45.1	81.8	101.1
6 TOLUENE (C_7H_8)	−26.7°	6.4	31.8	51.9	89.5	110.6
7 WATER (H_2O)	−17.4°	11.4	34.0	51.6	83.0	100.0
8 GLYCERINE ($C_3H_8O_2$)	125.5°	167.2	198.0	220.1	263.0	290.0
9 CESIUM (Cs)	279.0°	375.0	449.0	509.0	624.0	690.0

Table 4.1 Vapor pressure-temperature data for several common materials.

might compare the numbers A and B to the critical pressure of the substance, or to the triple-point pressure. If we do this, we get some correspondence but not good agreement (as we see in Table 4.2). Alternatively, we might ask ourselves, "What numbers do characterize the substance at the various points along the vapor curve?" Among the various properties we could list the molecular weight M, the latent heat of vaporization L, the specific heat C, and the volume occupied by the gas or by the liquid at the given pressure and temperature. If we try to form some mathematical function A(M,L,C,V) out of these variables we find that since the dimensions of A are those of a pressure, the possible functions A(...) are strictly limited.

Let us attempt to form a function A(...) by using a product of the variables raised to powers p, q, r, s, and t. Thus, we have

$$A = M^p L^q C^r V_{gas}^s V_{liq.}^t . \qquad (4.2)$$

Since the dimensions of the molecular weight are mass, (M) those of the latent heat are energy (that is, mass × length^2 × time^{-2}) per unit mass, those of the specific heat are energy ($M L^2 T^{-2}$) per unit mass per degree (°), and those of volume are length cubed (L^3), we can write the dimensions of A as

$$M^p\left(\frac{ML^2}{T^2} \cdot \frac{L}{M}\right)^q\left(\frac{ML^2}{T^2} \cdot \frac{1}{o}\right)^r (L^3)^s (L^3)^t . \qquad (4.3)$$

These must agree with the dimensions of pressure, namely, force per unit area, or (MLT^{-2}/L^2). Considering the

	$P_{critical}$	P_{triple}	A	B
1. NITROGEN	33.5 atm		4.6 atm	− 19.2 atm
2. OXYGEN	49.7 atm	54.34 atm	4.6 atm	− 20.3 atm
3. ACETONE	46.6 atm		4.9 atm	− 27.6 atm
4. METHANOL	78.5 atm		6.8 atm	− 39.0 atm
5. WATER	218.4 atm P = AlnT + B	.00603 atm	6.6 atm	− 38.2 atm

Table 4.2 Some additional vapor pressure data.

numbers p, q, r, s, and t as variables, we have the equation

$$MLT^{-2}L^{-2} = M^{p}M^{q}L^{2q}T^{-2q}M^{-q}M^{r}L^{2r}T^{-2r}(^\circ)^{-r}L^{3s}L^{3t}, \tag{4.4}$$

which simplifies to

$$M^{1}L^{-1}T^{-2} = M^{p+q-q+r}L^{2q+2r+3s+3t}T^{-2q-2r}(^\circ)^{-r}. \tag{4.5}$$

For Eq. (4.5) to hold, the exponents of M which appear on the right-hand side must be identical with those which appear on the left, and similarily for the exponents of L, T, and °. Thus, we have the equations

$$1 = p + r \tag{4.6a}$$

$$-1 = 2q + 2r + 3s + 3t \tag{4.6b}$$

$$-2 = -2q - 2r \tag{4.6c}$$

$$0 = -r. \tag{4.6d}$$

Proceeding from Eq. (4.6d) and substituting r = 0 in (4.7c) we have q = 1; substituting r = 0 in (4.6a) we have p = 1. From r = 0, q = 1, and (4.6b) we get

$$-3 = 3s + 3t, \tag{4.7a}$$

or

$$s + t = -1. \tag{4.7b}$$

Dimensional analysis has led us to expect that the constant A has the functional form

$$A = \frac{ML}{V}, \tag{4.8}$$

and so does B. The proper expression to use for the volume is uncertain since we have both V_{gas} and V_{liquid} to consider.

In the middle of the nineteenth century Rudolph Clausius examined the changes in P, V, and T, involved in transitions across the vapor pressure curve. The changes in pressure and temperature along this curve must be related by

$$\frac{\Delta P}{\Delta T} = \frac{ML(T)}{T(V_{gas} - V_{liq.})}, \tag{4.9a}$$

which may be transformed into

$$\Delta P = \left(\frac{ML}{V_{gas} - V_{liq.}}\right)\frac{\Delta T}{T}. \tag{4.9b}$$

This differential relation is a general property of the class of functions

$$P = \left(\frac{ML}{V_{gas} - V_{liq.}}\right)\ell nT + B, \tag{4.10}$$

which can be shown by the methods we used in the Tait equation. Dimensional analysis led us close to the explicit form of Clausius' expression.[14] The Clausius equation predicts the slope, $(\Delta P/\Delta T)$, of the vapor pressure curve at every point as a function of the latent heat at that point, the temperature, and the change in volume of the substance as it transforms from liquid to gas.

If a substance is kept below the melting point it is found that vapor is also present. This process of a solid changing directly to the vapor is called sublimation. A solid-gas vapor pressure curve can be obtained for the substance much like the liquid-gas vapor pressure curve which we examined earlier. The sublimation curve terminates at the triple point at its upper end and at the origin (P = 0, T = 0) at its lower end.

Experiment Sequence 23

The Clausius equation applies equally well to the sublimation curve.

[14] Often called the Clausius-Clapeyron equation, because Clapeyron developed the equation independently.

The meaning of the various terms, L, M, and $(V_{gas} - V_{solid})$ is analogous to the meaning in the liquid vapor equilibrium case.

4.2 FREEZING

There is also an equilibrium curve, and a Clausius-type relation among the variables, P and T, for the solid liquid equilibrium. The volume difference between the liquid and solid phases is so small that the melting point scarcely changes when the pressure is greatly increased, that is, the P(T) curve is very steep. Since most substances contract upon freezing, increasing the pressure on such materials in the liquid state will raise the freezing point. Water expands upon freezing so its freezing point is lower under pressure, $7.5 \times 10^{-3}C^{\circ}$ lower when the pressure is increased by one atmosphere.

Equilibrium can also occur between different solid phases. In ice the first solid-solid phase transition occurs at a pressure of 3000 lbs/in.^{2} and a temperature of $-22^{\circ}C$, where the hexagonal crystal structure coexists with a cubic form. Five more crystal modifications have been observed at still higher pressures (see Fig. 4.1).

Liquids can be cooled below the temperature at which they would normally freeze and are then said to be supercooled. A supercooled liquid is

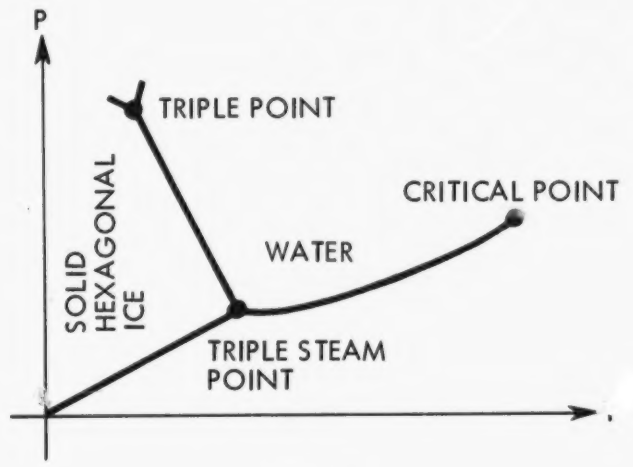


Fig. 4.1

in an unstable condition. The slightest disturbance is apt to start the freezing and quickly return the system to normal. The vapor pressure above the supercooled liquid has a definite value for each temperature and is shown in Fig. 4.1 by a dotted line. Superheating phenomena have also been observed.

In Chapter 2 we discussed the description of substances in terms of pressure and volume when the temperature is fixed. Now we have seen a description in terms of pressure and temperature for a fixed volume. The two descriptions can be combined into one if we construct a three-dimensional space with coordinates P, V, and T. We show some typical examples in Figs. 4.2 and 4.3. The behavior of a fixed amount of the substance is now described as a surface in PVT space. At a given pressure and temperature, the

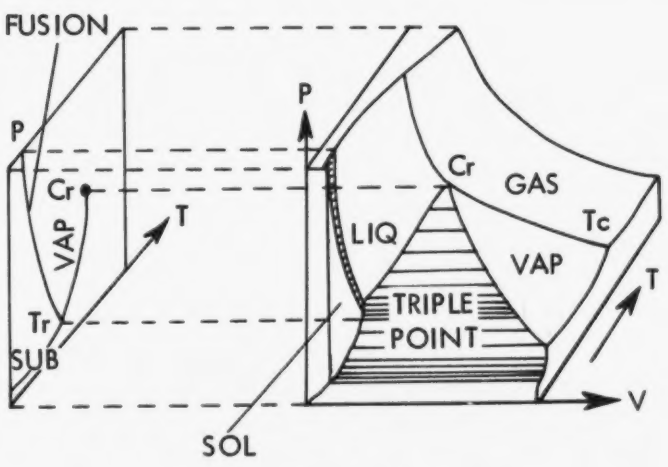


Fig. 4.2

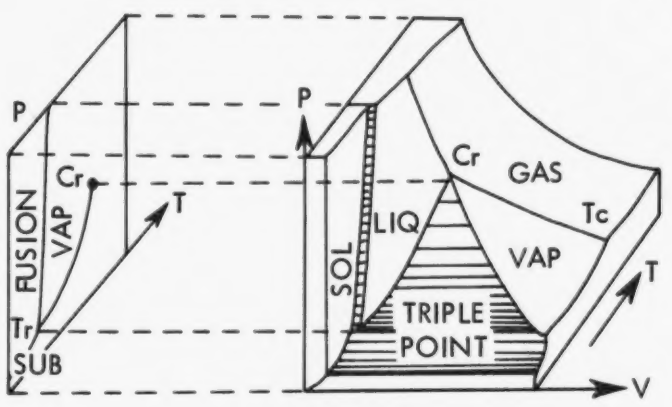


Fig. 4.3

volume of the system can only be increased by adding more material.

4.3 PHASE DIAGRAMS

We have chosen so far in our study of matter to limit our attention to pure substances. The phase diagram, in a modified form, can be used to describe the behavior of a mixture of two substances. When we consider such a mixture we must introduce a new variable into the description, namely, the composition of the mixture. To specify completely the behavior of such a mixed substance requires four dimensions; pressure, temperature, volume, and composition. However, we will assume a fixed volume of material held at a fixed pressure. Then we can describe the thermal behavior of a two-component system by selecting the temperature and the fractional composition as variables. When the fractional composition is used as a variable the composition coordinate can be scaled from left to right in terms of percent of component kA and, equivalently, from right to left in terms of component B. Figure 4.4 illustrates such a diagram for a mixture of methyl alcohol and water. One hundred per cent water is represented at the right end of the diagram, 100% alcohol at the left. The lower line on the diagram represents the boiling temperature of a mixed liquid of that composition. We have drawn Fig. 4.4 for a pressure of one atmosphere although a similar diagram could be drawn for any pressure. We see from the figure that pure alcohol boils at 65°C and pure water boils at 100°C. at one atmosphere pressure. The boiling points of the various mixtures lie between these values. For example, a 50-50 mixture boils at about 76°C.

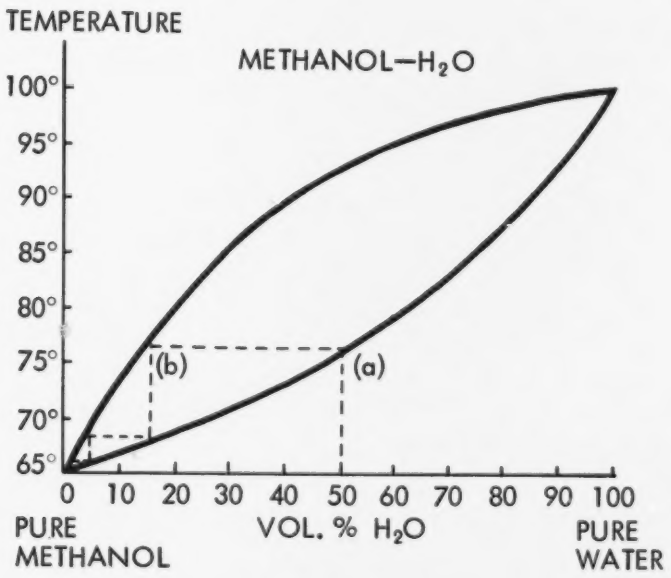


Fig. 4.4

Now consider the mixed vapor. The upper line in Fig. 4.4 shows the temperature dependence of the vapor composition at one atmosphere which is in equilibrium with liquid at the same temperature. The two curves coincide at the end points but, because they differ in the region between, it is possible to use the evaporation properties to separate the components of the mixture, a process we call fractional distillation.

A mixture of alcohol and water may be separated by distillation. Suppose we have a mixture of 50% water and 50% alcohol. We heat the mixture to a temperature of 76°C and find that the vapor at this temperature is 15% water and 85% alcohol. If we remove and condense the vapor, the remaining water-alcohol mixture has a new composition richer in water. Its vapor will also be richer in water than the first condensate was. The separated first condensate containing 85% alcohol may be redistilled, yielding a second condensate of composition of about 5% water and 95% alcohol. The process can be repeated indefinitely, leading to as low a concentration of water as is desired.

Typical distillation equipment has the various boiling and condensing regions arranged in the form of a column. A mixture is introduced at the bottom and purified material removed at the top. Such a distillation column is illustrated in Fig. 4.5. Modern distillation devices are rated in units of "plates," a term which describes the effect of one evaporation-

condensation step. Some highly efficient devices contain 100 or more effective plates.

When only one phase of a pure substance is present, the values of two variables (P and R, or P and V, or V and T) may be chosen arbitrarily. If more than one phase is in equilibrium, the number of variables that may be chosen freely is reduced. If more than one substance is present, the number of "free" variables is increased. In 1876, J. Willard Gibbs formulated a quantitative relation called the phase rule:

$$P + F = C = 2,$$

where C represents the number of components present in the system and P represents the number of homogeneous phases which are simultaneously present. The number of variables is F; for example, pressure or temperature which may be freely chosen. In a mixture of ice, water, and steam, there is one component and three phases; thus C = 1, P = 3 and we compute F to be zero. There is no freedom in selecting the conditions since we are at the triple point. If we add salt to an ice and water mixture, we now have two components and we might expect four possible phases (solid salt, salt in water solution, solid ice, water vapor). Since this leads to F = 1, we conclude that the four phases cannot coexist. Any three of them can occur together and each possible triplet (there are four), leads to a triple point in the phase diagram. If some one additional property of the system (such as an electrical, magnetic, or optical property) is also varied, we would replace the 2 with a 3. We may see the essential features of Gibb's result by examining the geometry of the phase diagram in P, V, T space.

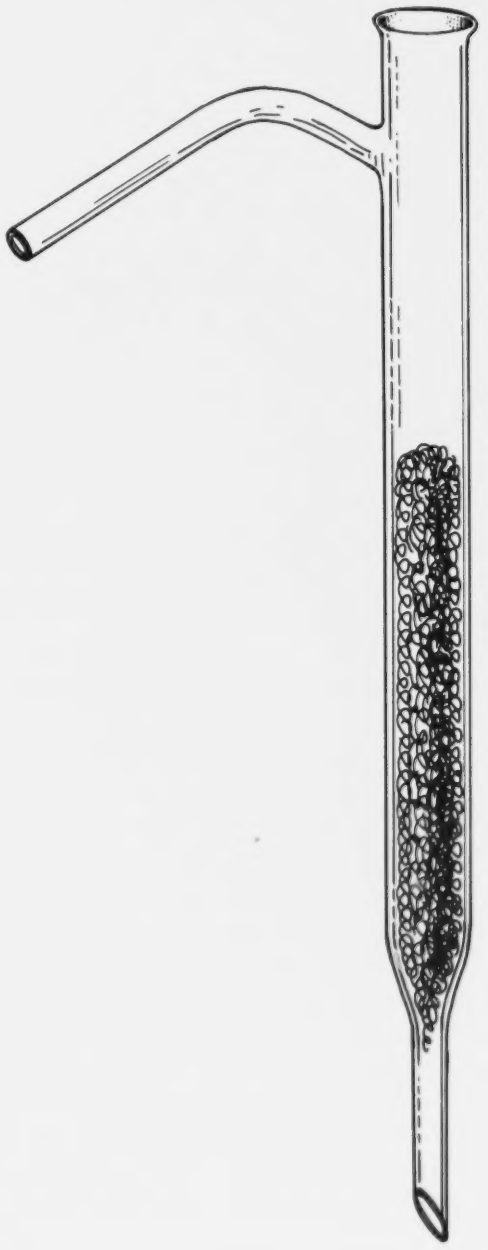


Fig. 4.5

The intersections of the various parts of the surface lead to lines and points. Gibb's rule predicts two degrees of freedom in selecting points on the surface, one in selecting points along a two-phase line and no freedom at all at the various triple points.

PREFACE TO THE EXPERIMENTS

These experiments are designed to be interesting and pleasurable for you. Their objective is twofold. First, you should learn something about the behavior of matter under various conditions and in various forms. Second, you should develop skill in using apparatus effectively to learn facts about nature. The experiments which are described here are graded in difficulty and subtlety from very simple to quite complicated. In many cases the interesting information is obvious; in others, you will need to obtain and record a precise numerical value. Some of the most interesting properties of matter reveal themselves only in the behavior of small changes in these numbers which are overlooked when the observer is careless.

Numerical data is often effectively displayed in graphical form. When a set of numbers A depends on a set B we say that A is a function of B and write A(B), read "A of B." When Cartesian coordinates are used to plot a graph of A(B) the functional relationship appears as a form of geometry. Whenever possible use the graphical method to display the functional dependence observed in your experiments.

Physical measurements usually are obtained by reading a scale of some kind. The scale may take the form of a ruler or meter stick, a thermometer, a dial, or a watch. Instruments almost always have a scale in which numbers are displayed along a line or around a circle, thus reducing the measurement to an observation of a length or an angle. It also happens, however, that sometimes the quantity that the instrument is measuring is not really the quantity you intended it to measure. For example, if you use a meter stick to measure the length of a bar and then again to measure its length when heated, you must take care not to heat the meter stick as well. It is quite possible that the heated meter stick will expand as much as the heated bar and leave you with the conclusion that heated objects do not expand at all. In each experiment ask yourself carefully what property the instruments are really measuring.

Because laboratory experiments are an activity of discovery the experimenter is never really sure what is going to happen next. He cannot even be sure which events matter and which are immaterial. It is good practice therefore to keep a sort of diary in the laboratory. Record not only the numbers obtained from your instruments but also any comments or observations which you think might be pertinent. When the experiment is completed you will be better able to decide which of your observations may be ignored and which are important.

Do not limit your use of the apparatus to the investigations proposed If a question occurs to you which the apparatus can answer, perform that experiment or observation, too. It is quite possible that you will discover facts or relationships which are not mentioned in the text, which may not even have occurred to the author.

There is seldom any point in trying to get the "right answer" in an experiment. More can be learned by trying to understand why your numbers may have disagreed with those obtained by other, more experienced observers.

EXPERIMENT SEQUENCE 1. PRESSURE IN A LIQUID

With the apparatus provided it is possible to measure the pressure exerted by both air and liquid. For the time being you must assume that the calibration of the various gauges is correct. You may use the large pipe full of water both open and closed at

the top. When the pipe is closed, air under pressure may be applied to the system with the bicycle pump. The long copper tube can be used to blow bubbles under water. The gauge at its end records the air pressure applied to the bubble.

Arrange the apparatus however you like but use it to investigate the pressure in the system.

Data should be recorded in the fashion of a diary. Write down everything you observe that seems interesting and pertinent. Be careful to record numbers and dimensions with your observations. The resulting data is best summarized by plotting and drawing graphs: for example, of pressure as a function of depth.

Compare your results to those of others using different liquids. On what property of the liquid does the pressure behavior depend? Does the pressure have a direction in the liquid? Compute from your data the weight of one cubic foot of the liquid.

Why are water storage tanks placed on hilltops?

Why is a submarine limited to depths less than 1000 feet?

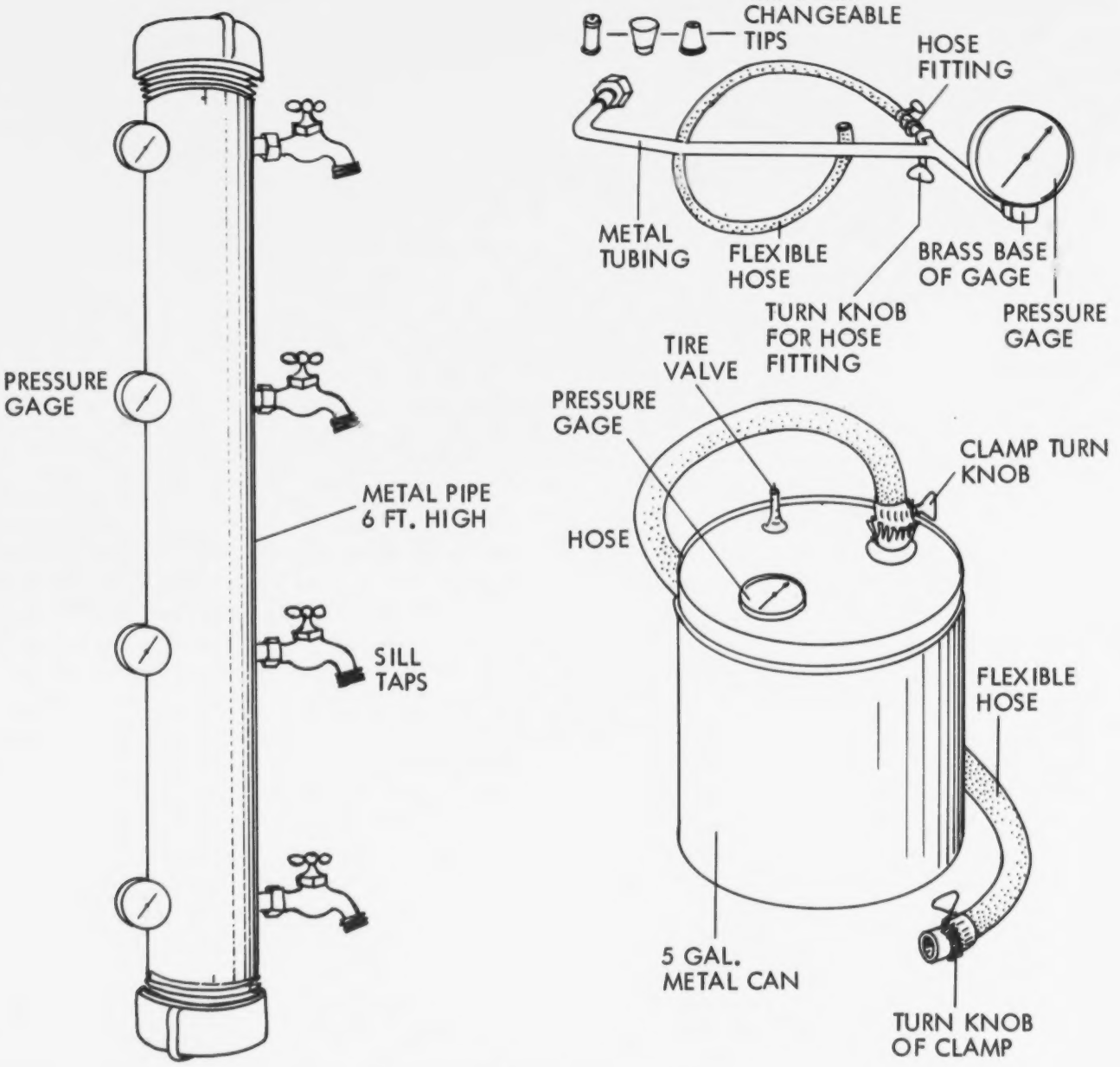


Fig. 1 [Experiment 1 (1)]

EXPERIMENT SEQUENCE 2. PROPERTIES OF AIR AND THE VACUUM

With a small quantity of water in the plastic tube open the stopcock to fill the flask with air, then close it. Take the apparatus to various places in the "sea of air" and observe the behavior of the water column.

Consider carefully how the water column functions as a pressure gauge.

Remove as much air as possible from the flask and repeat the experiment. You are free to improvise as much as you like here.

Connect a garden hose to the plastic tube so as to extend it and use it as a pressure gauge to measure the pressure of the atmosphere. The air should be removed from the hose by filling it with water, then capping it tightly. Use a rope to lift the filled hose as high as possible; for example, by pulling it from the ground up to a high window. The atmosphere now supports the column of water. Observe carefully the behavior of the column when it is 20 or more feet above the open bore of the flask.

The experiment is interesting if repeated with a more dense liquid.

How deep is the ocean of air, that is, in amount of air, not in height?

Why do bubbles form in the hose as the vacuum condition is approached?

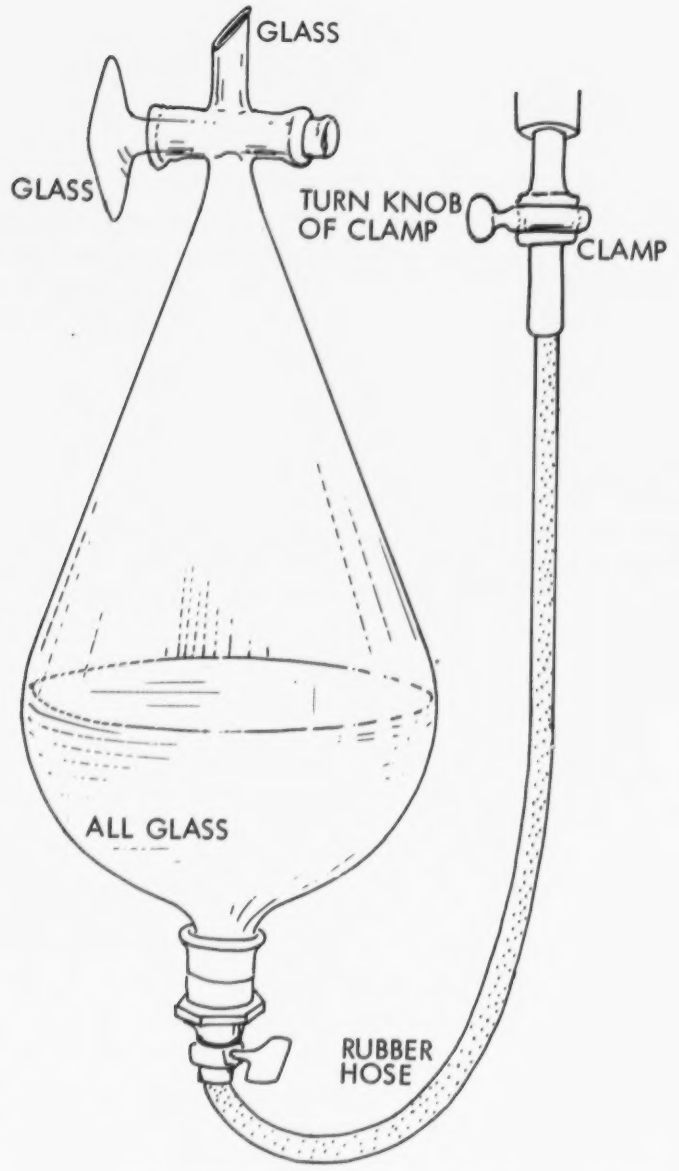


Fig. 2 [Experiment 2 (1)]

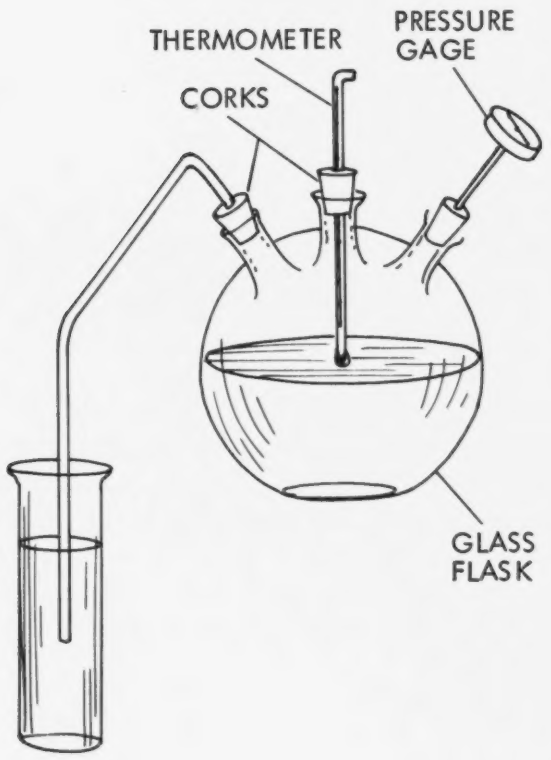
EXPERIMENT SEQUENCE 3. COMPRESSIBILITY OF AIR AND WATER

Put a fixed quantity of air into the system and close it off. Now vary the volume and the pressure and so determine the functional relationship P(v). Note the thermometer readings carefully. If the volume is changed suddenly, fluctuations may occur indicating that the process is not isothermal. It is useful to use several different gases. The resulting data should be displayed graphically. Compare the presentation of the data when gauge pressure is plotted to the data when absolute pressure is plotted.

To study the compressibility of water fill the small pipe cylinder and close it tightly. For best results remove all the air from the system. Air may be dissolved in the water so distilled water is best.

Compress the water by turning the end cap with the wrench. You can compute ΔV from the angle of turn and the advance of the screw thread. Plot ΔP (ΔV) and estimate the compressibility.

Calculate the compressibility of air from your data. Can you estimate the height of the earth's atmosphere from this and earlier data? Call the



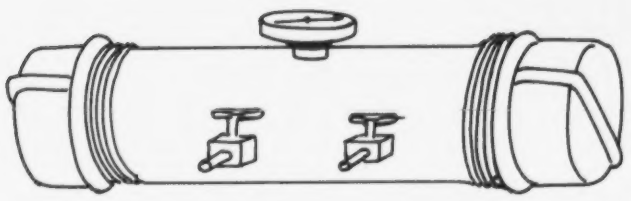


Fig. 3 [Experiment 3 (1)]

top of the atmosphere the height at which the pressure is 1/100 th of that at sea level.

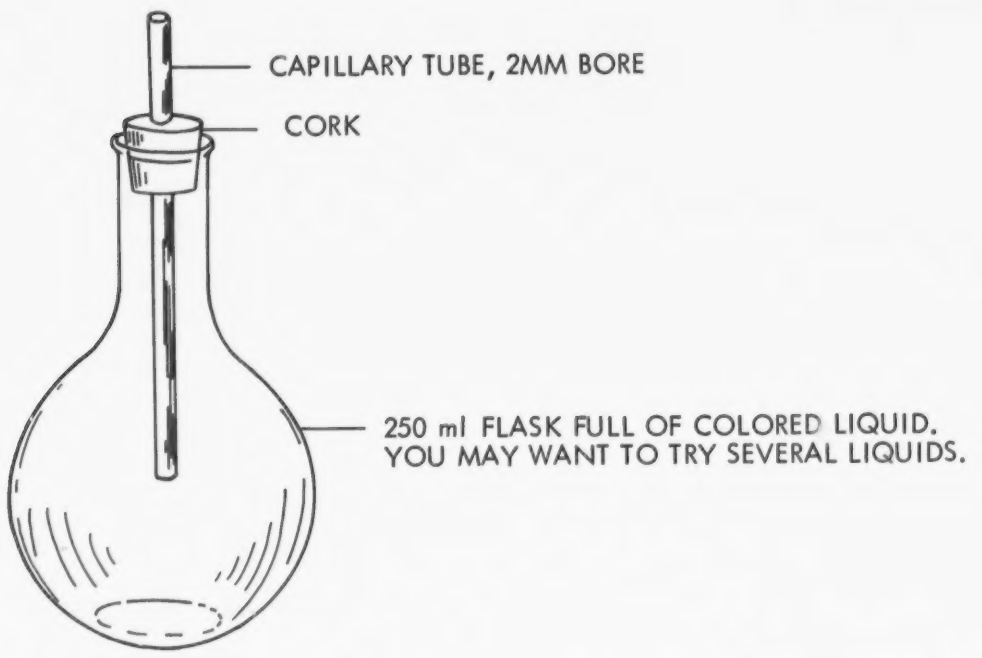
EXPERIMENT SEQUENCE 4. TEMPERATURE SCALES

The purpose of this experiment is to attempt to construct a temperature scale, particularly to locate the 50° point.

Select a quantity of substance at 0°C (the temperature of a melting ice-water mixture) and an equal quantity at 100°C (the temperature of boiling water) and mix them. A thermometer may be used to observe the temperature of the mixture but do not take the scale literally. Simply use it as a reference or marker. Use several sample substances such as water, metal, alcohol, xylene, and amyl ether. Do <u>not</u> use a bunsen flame around these materials as they are flammable. Also do not breath the vapors.

After determining a midpoint (50°) extend the technique to define the quarter and three-quarter points, etc.

Discuss the implications of the experiment. You might suggest other ways of defining the 50° point.



EXPERIMENT SEQUENCE 5. TEMPERATURE SCALES

Use the expansion in length of a metal bar to determine the 50° point. As in Experiment 4, measure the length at 0°C and at 100°C and use this information to define 50°C.

Determine the 50° point by using the expansion of a liquid. The apparatus is sketched below. The flask may be immersed in water at 0°C and 100°C to determine the fixed points.

What effect does the expansion of the glass have?

How does the 50°C point determined in this experiment compare to those obtained in Experiment 4?

If the flask is filled with water, is the 50°C point as defined here the same as that defined by mixing equal amounts of hot and cold water?

INSTRUCTOR'S GUIDE TO THE EXPERIMENTS

In this monograph experiment and text are closely interwoven. The experimental material is designed to give the student some experience with a wide variety of thermal and material phenomena. The text is intended to be read and used without formal classroom work. Of course, an instructor should be available to answer questions. Similarly, the experiments are designed to be performed with a minimum of supervision. One of their purposes is to teach the student to examine nature by using apparatus to ask questions. The text has been so written that the student does not know in advance just what result to expect from an experiment.

Most of the experiments are designed to deliver information which can be graphed. The graphs, data, etc., which are acquired from the experiments are intended to supplement the written material in the monograph. It is frequently suggested that several gases or several solids be measured in a given experiment. When a large class is involved it is recommended that each pair of students select a different substance and then compare their results. Discussion among students at this point is valuable. The instructor should attempt to limit his interference to the correction of gross errors of fact or interpretation. The student should be encouraged to invent model systems of his own which accord with his data, rather than to be pressed too soon to use the models popular in contemporary physics. Experimental physics should encourage inductive rather than deductive thinking.

EXPERIMENT SEQUENCE 1. PROPERTIES OF PRESSURE

The iron pipe is six feet high and is equipped with four pressure gauges and four sill taps. The gauges shown in the photo are not very satisfactory but were all that were available to us on short notice. They are two-inch gauges made by the Marshalltown Mfg. Co. and have a range of 30 psi with a least count of 1 psi. Unfortunately the first division is 2 psi since it requires 1 psi to move the pointer away from zero. More suitable would be gauges with a least count of 1/10 psi and a range to 15 psi. The hoses are equipped with conventional hose fittings; Schroeder service station hoses and fittings would be even more suitable. These devices have a simple lock-ring construction permitting quick changes.

The pneumatic tank shown is a strong five-gallon can with pressure gauge, hose fitting and bicycle pump fittings attached.

The probe is a small copper tube equipped with a pressure gauge and hose at one end. The probe tips should be attachable easily to permit the probe to be used to investigate the effect of pressure on the size of the opening, and on orientation in the liquid. The air pressure necessary to form a bubble at various depths is observed. The pressure gauge used here has an expanded scale at the lower end with a least count of .1 psi. It is excellent for the task. The gauge was made by U.S. Gauge Co. and is three inches in diameter. Its only identifying mark is the number 17132 on the dial.

EXPERIMENT SEQUENCE 2. PROPERTIES OF AIR AND THE VACUUM

The flask with a volume of about a liter is connected to a plastic U tube filled with water to measure the internal pressure in the flask. The stopcock is opened to bring the pressure in the flask to ambient pressure

and then closed. When the apparatus is carried up and down stairs changes in the height of the water column are observed. The changes are small so the change in volume of the air is negligible.

After this initial experiment the student can attempt to remove the air from the flask and see how good a vacuum he can get. Finally a 35-foot transparent garden hose is attached to the flask. The hose and system are filled with water and the hose is sealed with a cap or plug at one end. The hose is pulled up the side of the building with a rope in an attempt to measure the pressure of the atmosphere. Because of air dissolved in the water, the vacuum obtained will be poor. It is interesting to see the air boil out of the water as the pressure at the top falls.

The instructor should construct a mercury manometer and demonstrate its use to measure the local atmospheric pressure.

EXPERIMENT SEQUENCE 3. THE COMPRESSIBILITY OF AIR AND WATER

This experiment is more or less conventional. One traps a quantity of air in a flask and measures P(v). As ordinarily performed, there is a large correction due to the 20-25 mm vapor pressure of water when water is used to change the volume. A low viscosity silicone oil with a low vapor pressure should be chosen instead. A mercury manometer is barely adequate for this experiment because its compliance is low. An aneroid pressure gauge, though perhaps slightly less accurate, is more suitable. If the volume and pressure can be changed rapidly enough, small but interesting temperature fluctuations can be observed.

A sketch of a sample apparatus arrangement is included. Although this experiment has not been tested at the conference, it is a routine experiment in many undergraduate laboratories and should offer no difficulties.

To examine the compressibility of water the apparatus shown in the photograph is used. A short length of three-inch iron pipe is fitted with a pressure gauge and two valves for filling. The end cap is rotated to apply pressure to the system. Of course, due to dissolved and trapped air, the compliance of the pressure gauge, the expansion of the iron, and the elasticity of the teflon tape used for sealing the pipe threads, the true value of the compressibility cannot be obtained. However, values of K as small as 5×10^{-5} psi have been observed ($K_{water} = 3 \times 10^{-6}$ psi).

EXPERIMENT SEQUENCE 4. TEMPERATURE SCALES

This experiment is intended to call out the difficulties in attempting to define the intermediate points of the temperature scale. By mixing boiling water and ice water in various proportions and observing the resulting temperature, the student examines the temperature scale. The mercury thermometer is to be used only as an indicator, not as a calibrated scale. Because of the problems of thermal insulation, good quantitative data should not be expected. This is an "intuitive" experiment.

Suggested mixtures are:

Ice water and boiling water
Ice and boiling water
Cold metal and boiling water
Cold and hot isobutyle alcohol, or xylene

In each case the starting temperatures are to be 0°C and 100°C. One must take care not to use a bunsen flame with xylene or alcohol.

This experiment has been tested and is effective in promoting thinking about heat capacity and temperature scales. Refrain from telling the student what is going on!

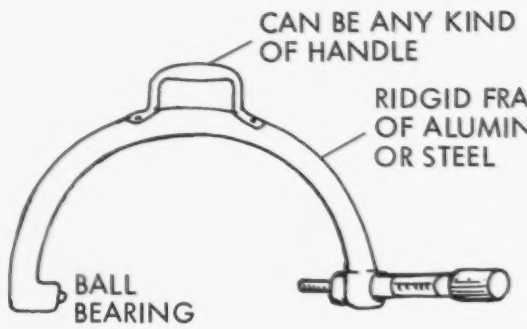
EXPERIMENT SEQUENCE 5. TEMPERATURE SCALES

In this experiment the relation between thermal expansion and temperature is examined. This experiment should contrast strongly with Experiment 4.

The first thermometer should be constructed from a 200-ml flash fitted with a capillary and a tight cork. A little washable red ink in the liquid makes it more readable, (Fig. Exp. 5.1). A 1-mm bore capillary is about right. Notice that if water is chosen for the thermometer the column goes down, then up as T goes from 0°C to 100°C, a dramatic effect but not very useful for a thermometer. Other liquids to be tried are alcohol, turpentine, acetone, glycerine, and mercury. Take care not to approach the boiling point of the volatile liquids.

Typical sensitivities are (not corrected for the expansion of the glass) 1 to 6 cm per degree depending on the temperature and the working fluid.

The thermal expansion of a solid should also be observed. The conventional apparatus with which I am familiar is too subject to errors due to thermal distortions of the frame. It is recommended that the sample be heated in a thermal jacket but that a large 50-cm caliper be constructed for measurement of the length. Since only differences in length are of interest, a conventional metric micrometer head can be attached to a simple steel frame. In this way the frame can be kept at room temperature. A sketch of the caliper is shown



This device is also useful in developing the familiarity of the student with the advantages of comparison or differential measurement. Notice that the use of a screw for measuring was first introduced in Experiment 3.

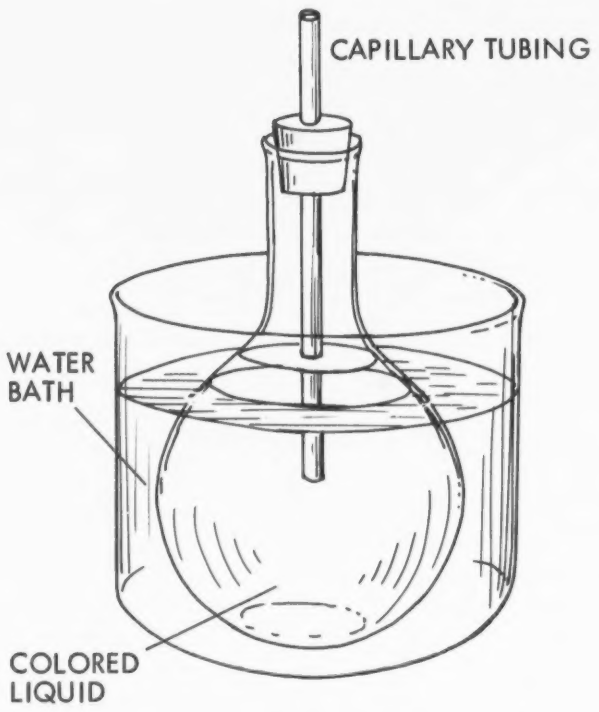
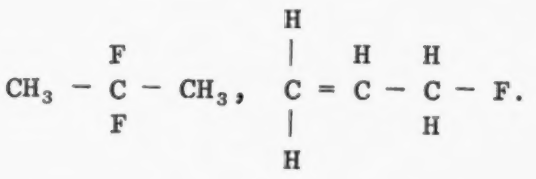


Fig. 5 [Experiment 5 (1)]

EXPERIMENT SEQUENCE 6. GAS THERMOMETRY

Construct a gas thermometer for measuring V(T). Experiments should be performed on air, neon, CO_2, and one of the freons. By measuring the volume of the gas at 0°C and 100°C one can define 50°C. Then set the volume for 50°C and adjust the water bath temperature to get this volume. The result is checked with the thermometer. The gases recommended are not all "well behaved" over this temperature range, especially the freons. The recommended fluorinated gases are:

$$Cl - \overset{\overset{Cl}{|}}{\underset{|}{C}}(F) - \overset{\overset{F}{|}}{\underset{|}{C}}(F) - F, \qquad CH_3 - CH_2 - \overset{\overset{H}{|}}{\underset{|}{C}}(H) - F,$$



Again it is recommended that a low vapor pressure silicone oil be used for a working fluid. Volume changes are most nicely read by observing the displacement of the working fluid in a calibrated cylinder as illustrated in the sketch.
By raising or lowering the beaker the pressure can be adjusted to atmospheric pressure throughout. This is a small correction. This experiment has not been tested at the conference but is a standard technique which should give no difficulty.

EXPERIMENT SEQUENCE 7. MEASUREMENT OF PRESSURE

This experiment is intended to measure P(T) at fixed volume. It may not be necessary for every student to perform both experiments 6 and 7. This experiment is a little more difficult than 6 if one wishes to avoid the use of a mercury manometer. If one starts with atmospheric pressure at 100°C then the pressure will fall to 555 mm Hg at 0°C. This is a drop of about 3 meters of water and militates against the use of a water manometer. An aqueous solution of thallium malonate or thallium formate can be made which has a density near 5 g/cm^3. Such a solution would be ideal for a manometer. In this experiment the column height would change on the order of 60 cm. We have performed no experiments with this material so we cannot attest to its use. The apparatus is sketched below:

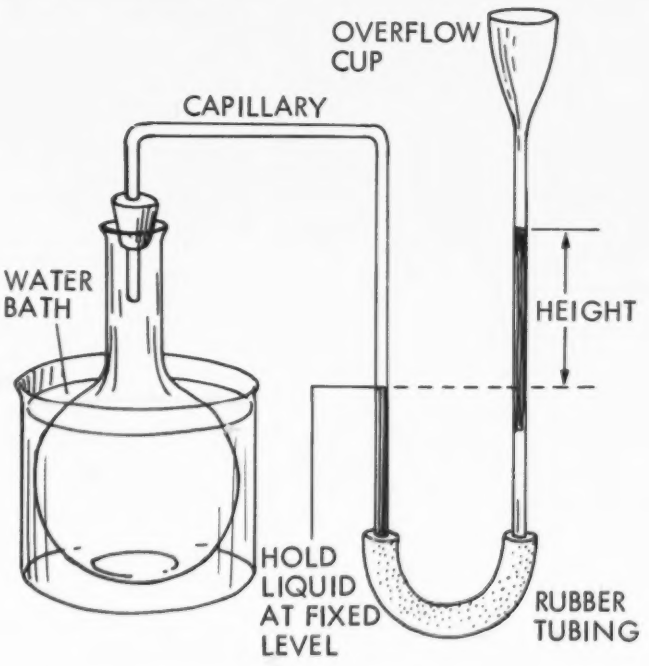


Fig. 7 [Experiment 7]

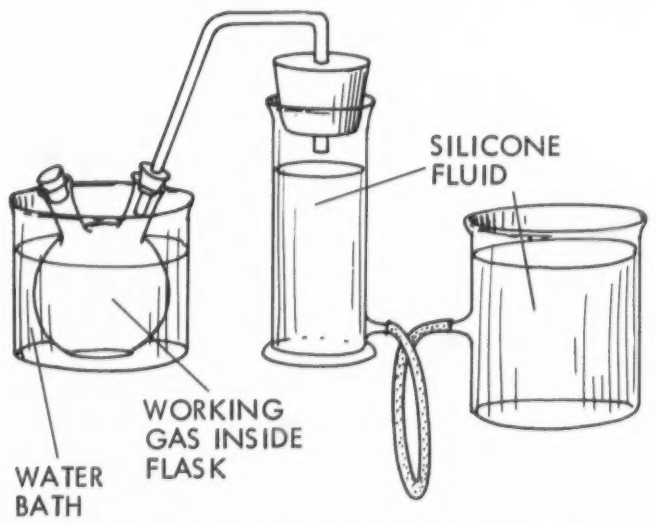


Fig. 6 [Experiment 6]

EXPERIMENT SEQUENCE 8. HIGH-PRESSURE BEHAVIOR OF GASES

This experiment is relatively sophisticated. It is intended that the student obtain P, V, T data suitable for estimating the virial coefficients and the van der Waals coefficients of several common gases such as air, CO_2, neon, etc.

The apparatus, which has not been built because of the time limitations of the conference, would be in the form of a bomblike cell capable of being filled to 100 atmospheres. The internal volume would be about 16 cm^3, permitting a PV product of 1.6 liter atmospheres, Since $B_p(T)$ is ~ 2 to 6×10^{-4} at 100 atmospheres and room temperature, the variation in PV is 2 to 6% over the working range of this instrument. We therefore can neglect

changes in the cell volume at pressure. If it is desired to calibrate the cell, this can be done by using a standard quartz cylinder as described further on. Note $C_p(T)$ contributes effects of the order of .1 to 2% over this range.

Experiments 8 and 9 are closely related and would use the same apparatus. A sketch of the cell appears below. The cell is machined of stainless steel as nearly symmetrically as possible. The ends can be capped with quartz plates for viewing purposes and also for calibration.

The internal dimensions of the cells are 2 cm diameter × 5 cm long. When a solid is introduced into the cell the working fluid volume will be about 1% of the chamber volume or 160 mm^3. The working pressure is 1 to 100 atmospheres.

For calibration a quartz cylinder with accurately ground and polished parallel ends is inserted in one chamber. Because of the quartz windows the cylinder can be observed from outside the cell. A gas laser is used to measure the change in length of the cylinder as a function of pressure by having the cylinder function as an interferometer. From the linear coefficient of compressibility the volumetric coefficient can be obtained and from this and measurement of the gas contained the true volume of the cell can be obtained as a function of pressure. The correction for cell volume is not necessary when working only with gases.

In measuring the PV product of a gas, the gas is allowed to expand from high pressure to atmospheric pressure and the expanded volume is measured. The high pressure can be obtained most easily by using commercial gases as supplied in high-pressure pressure cylinders. The calibration of the usual pressure gauges on such bottles is not known to the author, however, so there may be some difficulty in determining the high-pressure value precisely. Of course, some sort of strain gauge on the bomb could measure this pressure. Altogether, this is a difficult experiment but rather important since it points up departures from ideal behavior. This experiment is one that might be performed as a demonstration by the instructor.

EXPERIMENT SEQUENCE 9. COMPRESSION OF SOLIDS AND LIQUIDS

Using the dilatometer described under Experiment 8 we compare a solid sample to the standard quartz cylinder. Both chambers are raised to the same pressure then the gas is removed and its volume is measured at 1 atmosphere to obtain

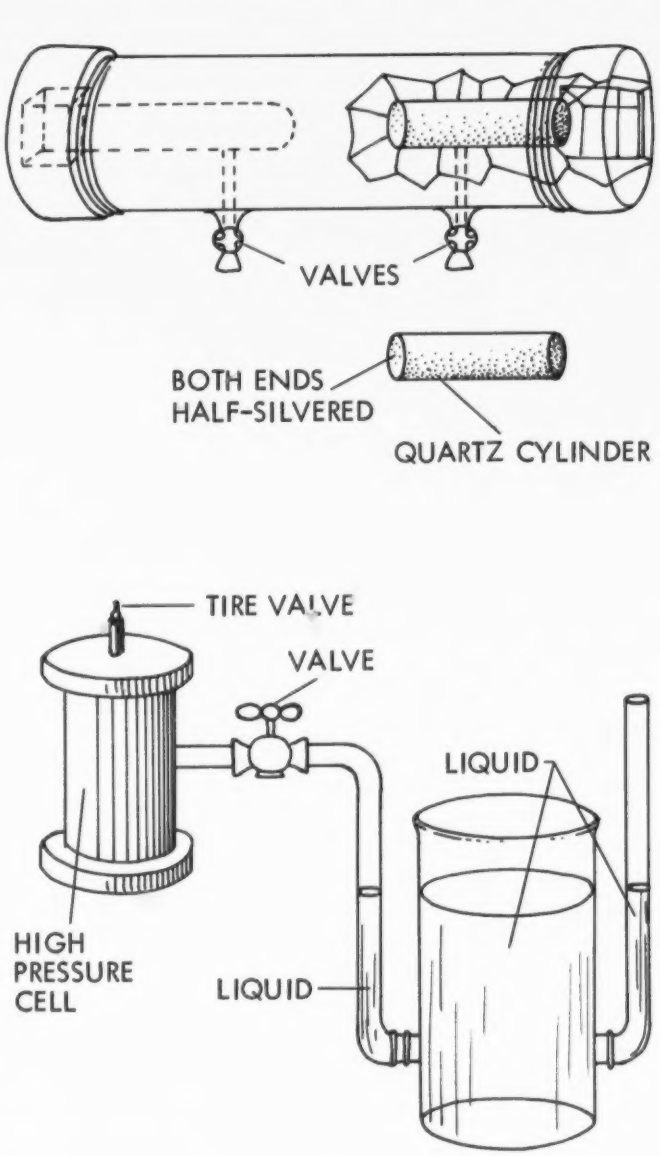


Fig. 8 [Experiment 8]

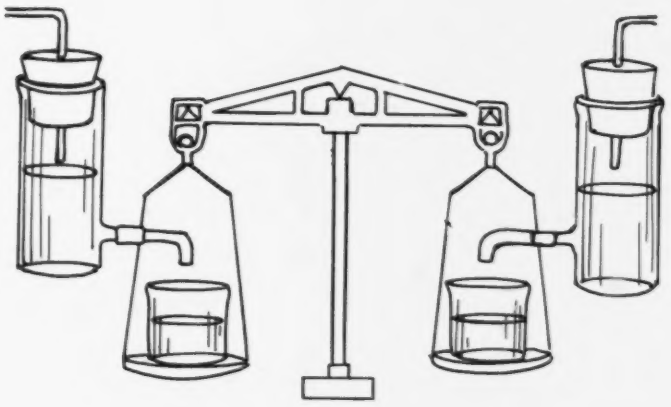


Fig. 9 [Experiment 9]

$$(V_1 - V_x) - (V_2 - V_s),$$

where V_1 and V_2 are the two sample chamber volumes. When the unknown and the sample are interchanged one measures.

$$(V_1 - V_s) - (V_2 - V_x).$$

The difference in these two measurements is $2(V_s - V_x)$. The volume differences $(V_1 - V_x) - (V_2 - V_s)$ and $(V_1 - V_s) - (V_2 - V_x)$ are obtained using a differential liquid displacement system as illustrated below.

Since expansion from 100 atmospheres will be 100 ×, about 16 cm^3 of liquid will be displaced. If one obtains a reading accuracy of 1 mg, about $10^{-5} cm^3$ differential volume change will be observable. Typical compressibilities are 1 to $5 \times 10^{-5} cm^3$ per cm^3 per atmosphere.

This experiment has not been constructed but should be straightforward to create and carry out. Liquids can be measured using this technique by containing them in plastic bags from which the air has been removed. The results will be less accurate because the samples will not fit the chambers as uniformly as specially prepared solid samples would.

EXPERIMENT SEQUENCE 10. CRYSTALLIZATION

For this experiment a melting stage microscope is required. Perhaps an inexpensive toy microscope could be fitted with a heat stage. It is important to measure the temperature of the stage rather carefully. The technique of examining substances near their melting points is a standard one for physical chemists. The temperature range should be room temperature to 200°C. An alternate stage with thermoelectric cooling down to about −40°C could also be valuable but more expensive.

This experiment is largely for qualitative observations. The sharpness of the melting point as well as the behavior of amorphous substances should be observed. Recommended materials are salol, Rochelle salt, $LiNO_3$, $CaI_2 \cdot 6H_2O$, NH_4Cl. Also other crystalline materials like table salt, and amorphous or plastic materials. One objective is to see crystallinity, hopefully samples of cubic, hexagonal, tetragonal, monoclinic, etc., forms.

EXPERIMENT SEQUENCE 11. YOUNGS MODULUS

The experiment is intended to measure Young's modulus for several solid specimens including a single crystal, a polycrystalline block, and a block of fused quartz. It is desirable to perform the experiment at various temperatures ranging from −70°K to +60°K. It is also desirable to show anisotropic elasticity on a single crystal if possible.

An optical interferometric method seems to be the only one adaptable to this problem. A gas laser is an excellent tool for this purpose and can be used in a simple arrangement with an optical wedge. A displacement of 5×10^{-5} cm can be easily observed by this method; for a 5 cm sample this is a strain of 10^{-5}. For typical materials this requires a stress of 10 K g/cm^2 which is quite reasonable. I envision samples with 1 cm^2 cross section.

The experiment has not been constructed so no test data are avail-

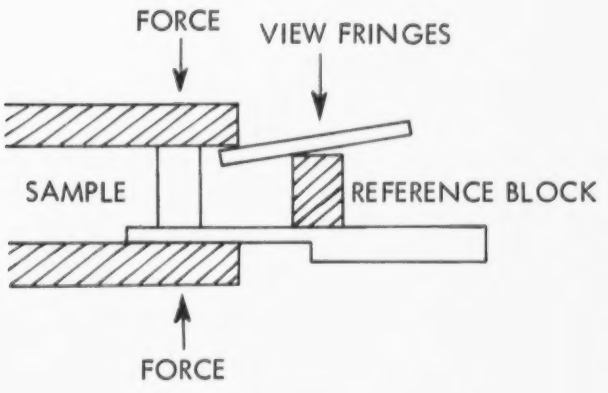


Fig. 11 [[Experiment 11]

able. The technique of applying the stress is a routine one common in mechanical engineering. It is recommended here that a hydraulic piston be used with a conventional pressure gauge. This avoids a consideration of static mechanics and supports earlier work on pressure. I have no comment to make regarding experiments with hot samples. Clearly this experiment needs to be constructed and thoroughly tested before use. It is important educationally that the temperature-dependent elastic properties and the anisotropic properties be observed.

EXPERIMENT SEQUENCE 12. CREEP UNDER MECHANICAL AND THERMAL STRESS

The wire is loaded to near the elastic limit and an electric current is sent through it. The clamps are thermal insulators. The wire itself is shielded against air currents by plastic spaghetti. The rate of fall of the heavy weight should be obtained as a function of temperature for various loads. It is important to obtain as nearly uniform a temperature as possible which is the reason for using a long wire. It is difficult to measure the temperature of the wire near its center without conducting excessive heat away. One method of doing this is to spot weld two tiny pieces of thermocouple wire perpendicular to the sample and bring them out through the spaghetti as illustrated. If the wires are fine they should not thermally

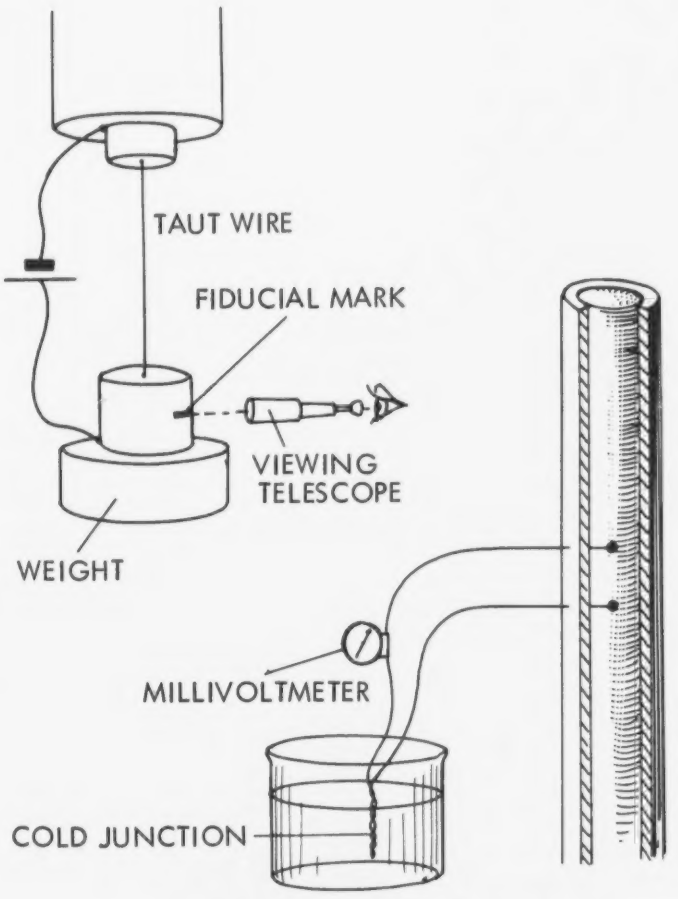
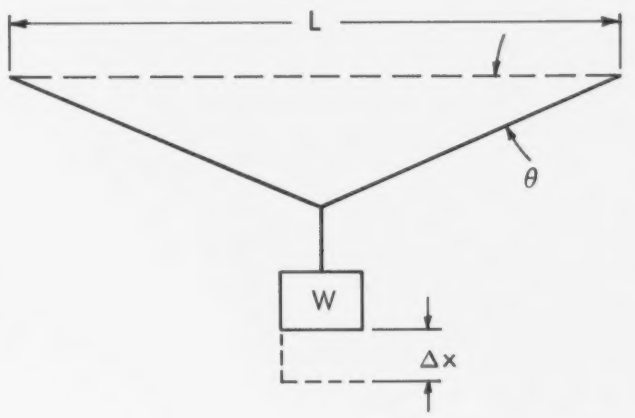


Fig. 12 [Experiment 12]

load the sample very much. This is the first experiment in the series in which a thermocouple is used for measurement of temperature. Perhaps a brief thermometry experiment at 0°C and 100°C with the thermocouple would be useful.

This experiment has not been constructed and so must be described as speculative.



EXPERIMENT SEQUENCE 13. PROPERTIES OF FIBERS

The elastic properties of amorphous materials are seldom measured in elementary laboratories. They provide a good contrast to the usual wires, etc. For this experiment we want to make the instrument compact so that it can be placed in a bath or chamber for temperature control. It is important, if reproducible results are desired, to avoid the use of spun materials which will unwind.

I believe this experiment can be done successfully by stringing a long piece of material over a set of ball-bearing pulleys in the manner shown. Since I estimate $Y \sim 10^8 g/cm^2$, for $P = 100 Kg/cm^2$, $\Delta L/L \sim 10^{-3}$; thus, a meter length will stretch 1 mm. We make a square array, go twice around, and the array is 5 inches on a side. The elongation is observed by the motion of the suspended weight. At equilibrium:

$$T = \frac{W}{2 \sin \theta}$$

$$\frac{\Delta L}{L} = \frac{1 - \cos \theta}{\cos \theta}$$

$$Y = \frac{T}{A\left(\frac{\Delta L}{L}\right)} = \frac{W}{2A} \frac{\cos \theta}{\sin \theta (1 - \cos \theta)}$$

$$= \frac{W}{2A \tan \theta \ (1 - \cos \theta)}$$

$$= \frac{W}{2A \ (\tan \theta - \sin \theta)}$$

$$\cong \frac{W}{2A \left(\frac{\theta^3}{2} \frac{\theta^5}{8} + \ldots\right)}$$

For small angles $\Delta x = \frac{L}{2} \theta$, so

$$Y \cong \frac{W}{A(\Delta x^3)}.$$

This apparatus is small enough to enclose in a vessel with the weight hanging out. Temperatures between

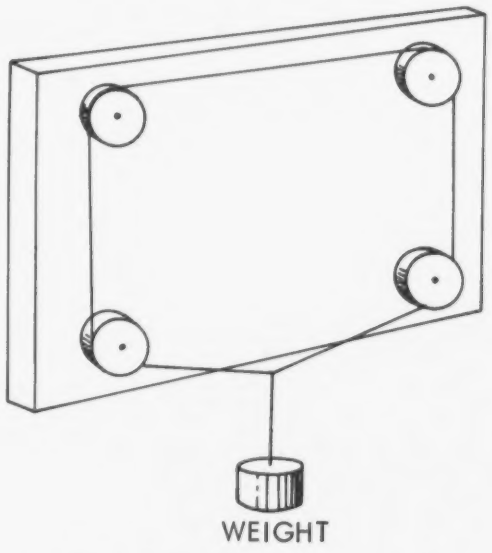


Fig. 13 [Experiment 13]

0°C and 100°C can then be obtained at the filament.

EXPERIMENT SEQUENCE 14. FLOW OF HEAT

In this experiment heat flow is balanced against water flow. The heat reservoirs are two large metallic cups fitted with bosses to clamp the sample rod firmly and in good thermal

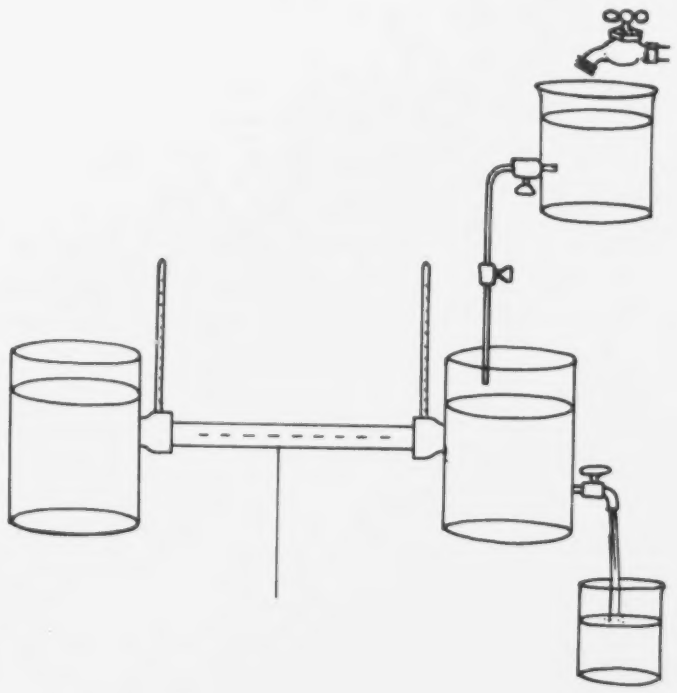


Fig. 14 [Experiment 14]

contact. Thermometers can also be mounted in the bosses. One cup is filled with water and maintained at 100°C. The second cup is fitted with an overflow pipe and cool water is passed through it. The cool cup and the sample and bosses should be insulated with polyfoam to reduce convection heat transfer. For best results the sample should be shiny and not touched by the polyfoam jacket.

Three experiments should be performed. First, the flow rate of water required to maintain the second cup at T_1. (The water source temperature is T_0.) Second, the rate of change of T_1 (i.e., dT_1/dt) when the water flow is stopped. Third, the rate of change of T_2, the hot reservoir when the flame is removed.

This experiment has not been tested here. However, it is a simple variation of an experiment successfully used at New Mexico State University and should give no difficulty in practice.

EXPERIMENT SEQUENCE 15. MECHANICAL EQUIVALENT OF HEAT

In this experiment the kinetic energy of a large flywheel is to be dissipated by magnetic induction of current in a copper disk. The flywheel can be typically 4 cm thick by 12 cm radius, with a mass of about 15 kg. The highest practical speed for such a wheel is about 3400 rpm or 360 rad/sec. The kinetic energy is then

$$KE = \tfrac{1}{2}(\tfrac{1}{2}MR^2)w^2$$
$$= \tfrac{1}{2} \cdot \tfrac{1}{2} \cdot 15 \times .12 \times .12 \times 360 \times 360$$
$$= 7000 \text{ joules.}$$

If this energy is put into a copper disk .125 cm thick × 12 cm radius, the temperature rise is

$$\Delta T = \frac{7000 \text{ joules} \times .24 \text{ cal/joule}}{8 g/cm^3 \times \pi \times 12 \text{ cm} \times 12 \text{ cm} \times .125 \text{ cm} \times .1 \text{ cal/gC}^\circ}$$
$$= \cong 114 \text{ C}^\circ.$$

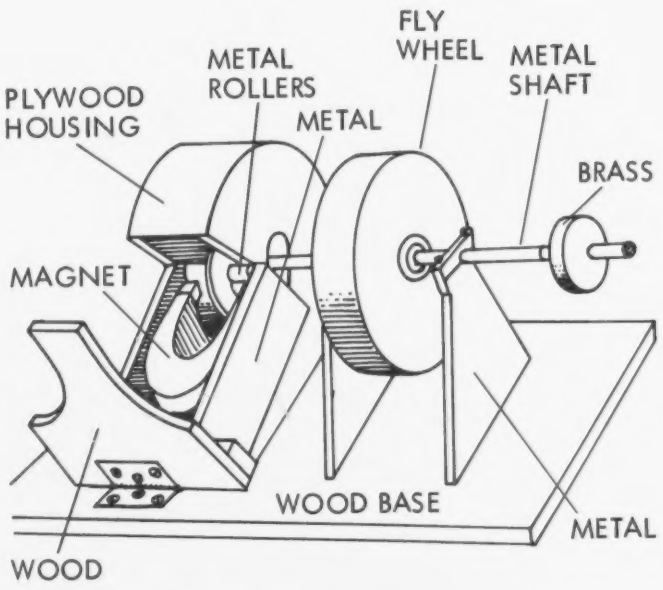


Fig. 15 [Experiment 15]

The impulse time is infinite because the induction drops as the speed drops. However, the initial torque can be calculated if the field is known. I approximate a formula for the torque as

$$T = \frac{\pi\sigma wtB^2\langle r^4\rangle}{2} \rightarrow 1000 \text{ newton-meter for copper at 5000 gauss.}$$

The stopping time is of the order of milliseconds. The approximations are obviously gross. Two to five seconds has been observed in the apparatus for fields of the order of 3000 gauss.

Two arrangements of the device are possible. In one the disk is coaxial with the flywheel and the magnets are external.

In the second system the magnets are rotated with the flywheel and the disk is external. A doorknob on the shaft would permit the student to generate the heat in his own hand as a demonstration.

A small hand motor such as a high-speed electric grinder fitted with a rubber wheel can be used to set the flywheel in motion.

We have assembled a model of the device and find that it works very well. The magnet is a magnetron magnet with cylindrical pole pieces about

2 in. in diameter and a gap of about $\frac{1}{2}$ in. The field strength is about 3000 gauss. Most of the stopping torque occurs in the first couple of seconds. Marks on the flywheel are used to observe the speed with a simple fixed-frequency stroboscope.

The copper disk must be carefully mounted to prevent heat loss to the shaft of the flywheel. Heat insulator and clamps do this very well. The copper disk must also be shielded against loss of heat to convection currents by cementing a thin layer of plastic foam to both faces of the copper.

The temperature rise of the disk is best measured by a thermocouple attached about halfway out toward the rim.

This experiment has been given preliminary tests at the conference and works well. Final testing is in progress at this writing.

Data Report for Experiment Sequence 15

		D^4t
Copper plate:	11 1/8 in. diam × .050 in. thick	
	Calculated C_p = 59 cal/C° = 247 joules/C°	
Inertia wheel:	Main wheel 9 in. diam × $1\frac{1}{2}$ in. thick	9842
	Brass knob 3 in. diam × 1 1/32 in. thick	83.5
	Brass clamps 4 in. diam × 5/16 in.	160
	less $2\frac{1}{2}$ in. × 1/16 in.	−2.5
	Copper disk 11 1/8 in. × 1/20 in.	732
	Shaft 3/4 in. × $12\frac{1}{2}$ in.	5
		10,830 in.^{5}
		or
		$1.07^4 \times 10^6$ cm^5

$$I = \tfrac{1}{2}MR^2 = \frac{\pi}{32}\rho D^4 t$$

$$I = .0829 \text{ Kg m}^2$$

For calculation

$$247\Delta T = 1.633\ \omega^2 \text{ where } \omega \text{ is in rev/sec}$$

With copper constantin thermocouple, wheel at 3900 rev/min

Observed .9 mv ± .1 referred to ~25°C (room temperature)
Gives 22C° temperature rise
Q_{heat} = 5434 joules
Q_{KE} = 6900 joules
Error = 20%

EXPERIMENT SEQUENCE 16. SPECIFIC HEAT OF LIQUIDS AND SOLIDS NEAR ROOM TEMPERATURE

This experiment requires an electrical heater of small mass with a power capability of about 50 watts. The one we use is simply a loose coil of nichrome wire which conducts about 6 amperes when connected to a 9-volt ac transformer. It should be placed in a styrofoam cup containing about 250 grams of water and ice. The temperature is now observed as a function of time. When the ice has melted the temperature will begin to rise. Above about 70°C the data are useless since considerable vaporization is taking place, even in a covered vessel. The vessel should now be permitted to cool, allowing calculation of the heat loss rate to the environment at each temper-

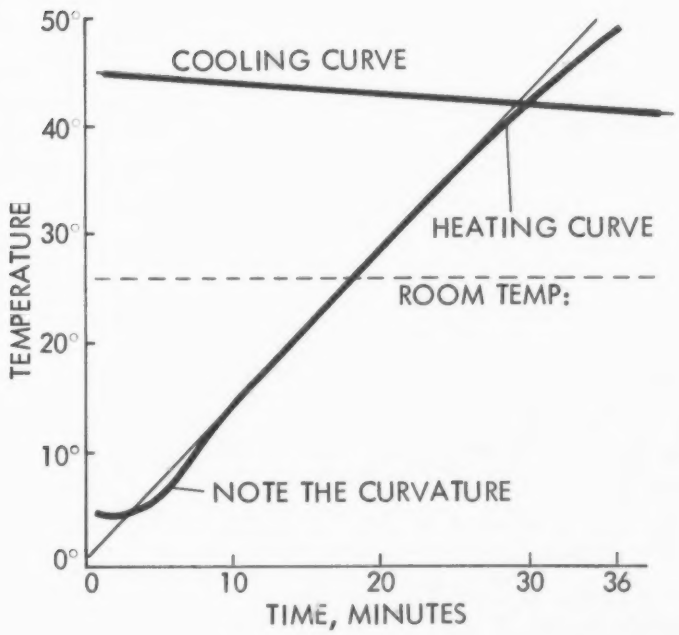


Fig. 16 [Experiment 16]

ture. The difference in rates can be used to plot $C_p(T)$.

This experiment has been performed and works nicely. Typical data are included below.

EXPERIMENT SEQUENCE 17. HEAT CAPACITY OF SOLIDS AT LOW TEMPERATURES

In this experiment we want to measure C_p for a metal from liquid air temperature to room temperature or higher. The temperature must be measured with a helium gas thermometer or a thermocouple. A similar experiment to the one described below has been performed by Professor Michaels of Bryn Mawr. The experiment described here has not been performed and needs to be tested.

The apparatus for this experiment is quite similar to that used for Experiment 16. The similarity is not accidental but serves an educational purpose. Also, the technique of taking warming or cooling curves is an excellent one for calorimetry. The sample should be a metal block, copper or zinc for example, fitted with a small electrical heater inside it. If the mass of metal used is 200 grams a power input rate of 10 watts is excellent. The temperature of the block will rise about 150° per minute. The metal block and heater are placed in a 500 ml flask which is used as the bulb of a helium gas thermometer. The flask is in turn placed in a styrofoam cup fitted with a lid, and the whole affair is submerged in liquid nitrogen. The styrofoam cup should be filled with helium also to prevent air condensation. The significant numbers are the power rate necessary to maintain a given temperature T and the rate of change of T, dT/dt, with full power on. The specific heat is calculated, as in Experiment 16 from the difference in the heating rate and the heat loss rate. The experiment is identical to Experiment 16 except that it is performed in an ambient environment at 77°K.

EXPERIMENT SEQUENCE 18 AND 19. HEAT CAPACITY OF GASES

There are several classical experiments (Rüchardt's, for example), for measuring Cp/Cv. For teaching purposes the measurement of Cp and of Cv directly is valuable. One way to do this is by discharging a capacitor through a fine wire. The pertinent numbers are as follows:

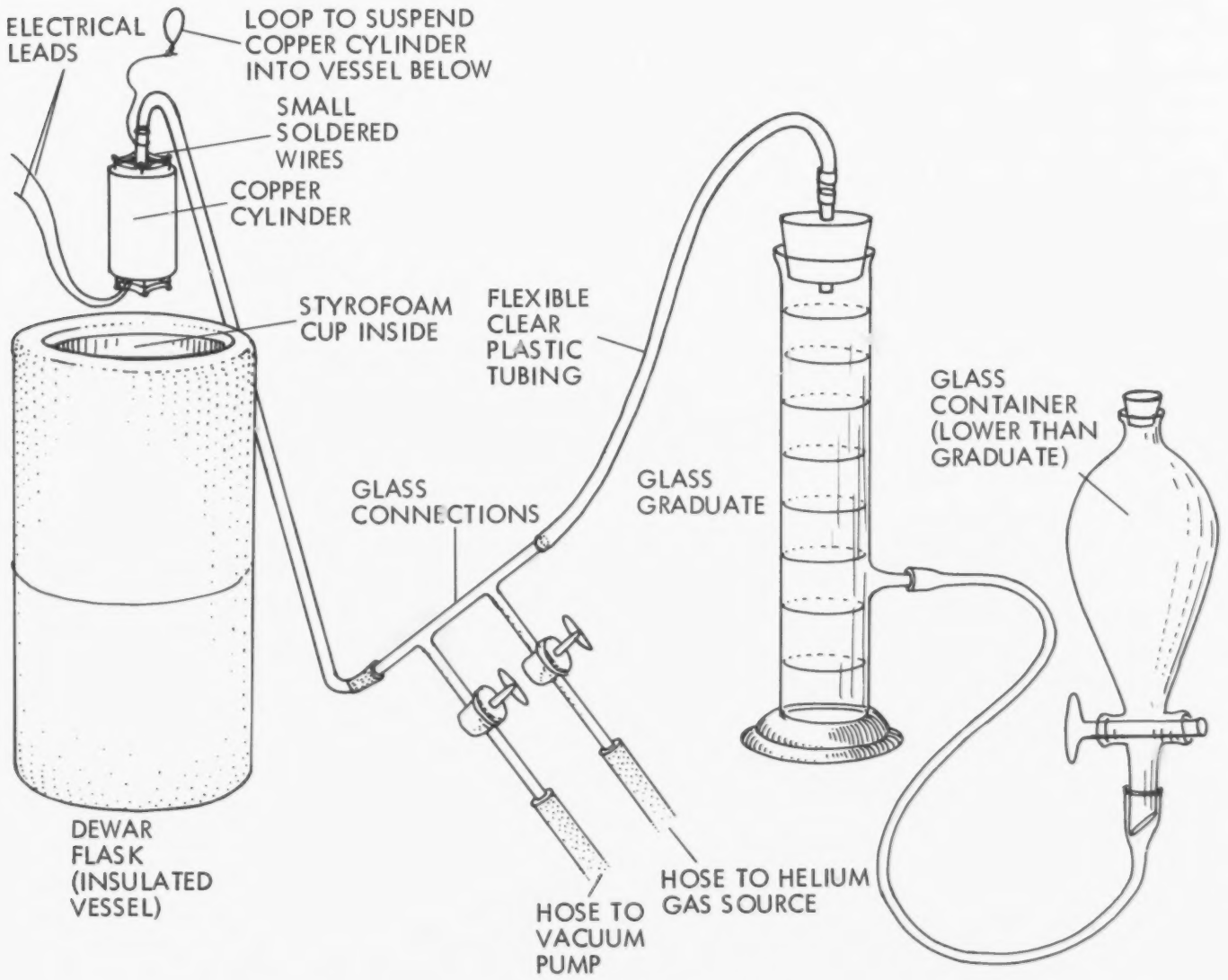


Fig. 17 [Experiment 17]

Ten meters of No. 36 nichrome wire weighs about 1 g, and has a resistance of 800 ohms. A 10 μF capacitor charged to 5000 V will release 125 joules into the wire in about 8 milliseconds. When a two-liter vessel at atmospheric pressure surrounds the wire the heat is delivered into $6\frac{1}{4}$ g of nitrogen gas (for example). The heat capacity of the gas is 25 joules/mole$^\circ$ or 5.6 joules/C$^\circ$ for this sample. This is much larger than the heat capacity of the wire (0.5 joule/C$^\circ$). The temperature rise of the gas is estimated to be about 20C$^\circ$ and can be observed with an ordinary thermometer or with a critically damped manometer for C_v.

After considering this scheme, a more promising alternative suggests itself. An ordinary flash bulb is stripped of its glass envelope and fired within the vessel. The total mass of metal introduced must be kept small. The energy release will be on the order of 500 joules or more per gram of burning wire so very little wire is needed. To calibrate the heat input, a whole battery of flash bulbs can be fired in a water calorimeter.

The uniformity of the heat released from the flash bulbs is unknown at this writing, so much testing must be performed before the experiment can be used.

In order to measure Cp the flask is fitted with a plastic bag which communicates with the pressure of the atmosphere. The volume of the bag should be of the order of 500 cm^3

since volume changes of the order of 25% are anticipated. The latent heat of melting ice is measured using a dilatometer method. The apparatus is illustrated. Observation is made of the height of the water column versus time with electrical power off and on. It is important that the vessel be inflexible to prevent changes in volume due to changes in pressure. In the apparatus illustrated a mason jar was surrounded by 2 in. of styrofoam. The inside diameter of the column was $\frac{1}{4}$ in. The heater is a length of nichrome adjusted to operate at six amperes on nine volts. The ambient power input was five watts, corresponding to about 18 cm/h fall in the water column. A graph of typical data is attached.

The entire apparatus can be placed in a pail which is put into a tub of ice water. With these added precautions the ambient heat input should be negligible, except for approximately one watt which comes from warming the water which descends from the column.

Earlier experiments with a paint can gave more precise but less accurate data. The precision was better due to the lower heat capacity of the can but the bulging of the can under the little bit of pressure applied destroyed the accuracy. A special spherical vessel with thin walls would be ideal. An alternate way of doing the experiment is with a calibrated plunger to displace liquid as the ice melts. In this way the pressure can be kept constant and the problem of warm water which comes from the column can be eliminated. Some further work should be performed to perfect this experiment.

We are also doing experiments in an effort to supercool a vessel containing water. If we can achieve 5C° of supercooling we shall then observe the expansion of the system as the ice forms and the temperature rises to 0°C. Although we expect this to be less accurate than the melting data it is a nice variation on the method of obtaining the latent heat.

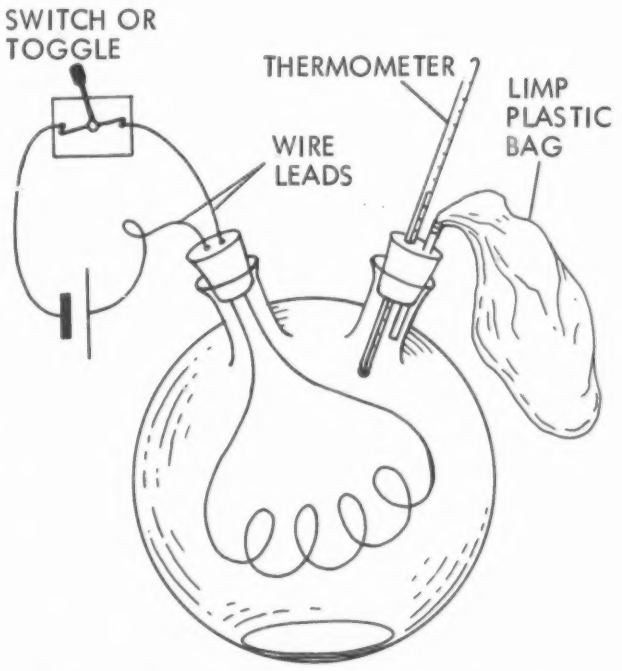


Fig. 18, 19 [Experiments 18, 19]

EXPERIMENT SEQUENCE 20. MELTING AND BOILING

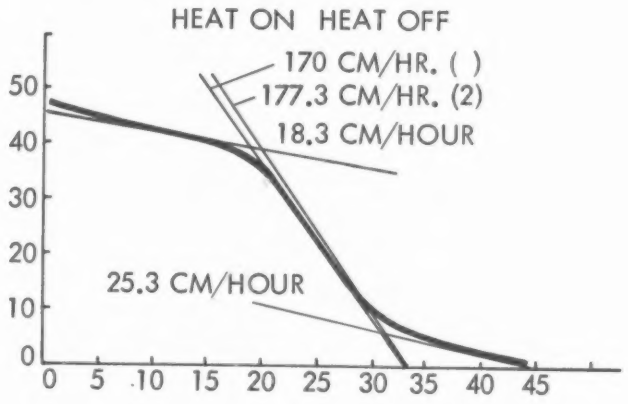
For measurements on latent heat we repeat the earlier technique on specific heat. We use a calibrated heater and place the apparatus on a pan balance to observe the rate of loss of mass. Several volatile liquids can be used (provided they are nontoxic) including liquid air. To calibrate the system the heat-loss rate must be measured. The easiest way to estimate the heat-loss rate is to use a nonvolatile liquid in the system and measure the heat necessary to maintain the system temperature at the point desired. When the sample liquid is used the heat of vaporization is so large that the correction due to conduction is masked. Vaporization can be prevented by using a pressure vessel but some complication and hazard ensues.

When measuring at liquid air temperatures it is best to use two different electrical heat input rates and subtract to eliminate the effect of heat conducted through the walls.

In the liquid air experiment the cold gas must be carefully discharged

to the atmosphere without imparting an impulse to the balance. The discharge pipe should be heated with a lamp to prevent the accumulation of frost.

In order to bring the electrical connections to the balance plate, the wires can be mounted near the central knife edge. If carefully done the torque imparted to the balance by the wire connections can be made negligibly small.



Data Report for Experiment 20

Supercooled water:
1-liter mason jar
1/8 in. brass plate for cover
rubber gasket
V = 1000 ml ± 10
ΔH = 9.95 ± .05 cm
T = −4°C ± .25
i.d. of tube = .252 in.

Cross section of tube = .317 cm^2

$\Delta V = 3.15\ cm^3$
11.06 g of ice changes the volume by 1 cm^3

Therefore, we froze 34.8 g of ice
Heat provided was 4000 cal

$$\therefore L = \frac{4000}{34.8} = 115\ cal/g$$

Accepted value = 80 cal/g
Error = 44%

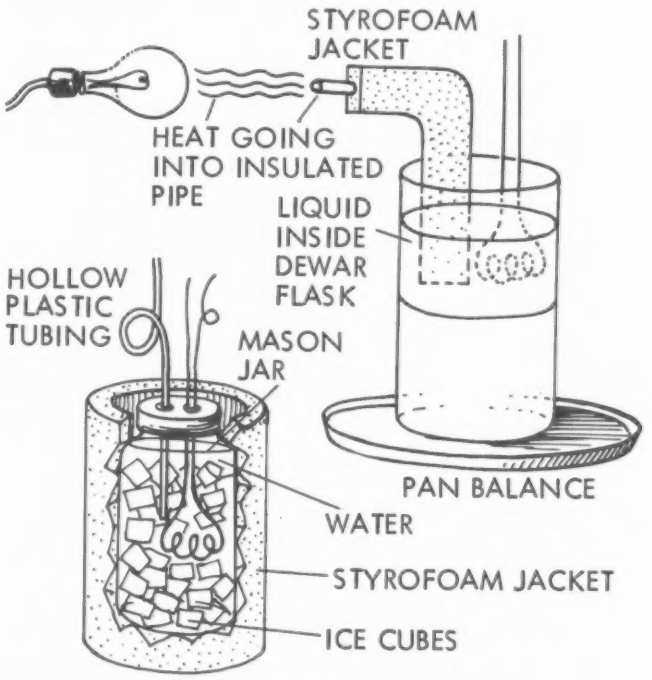


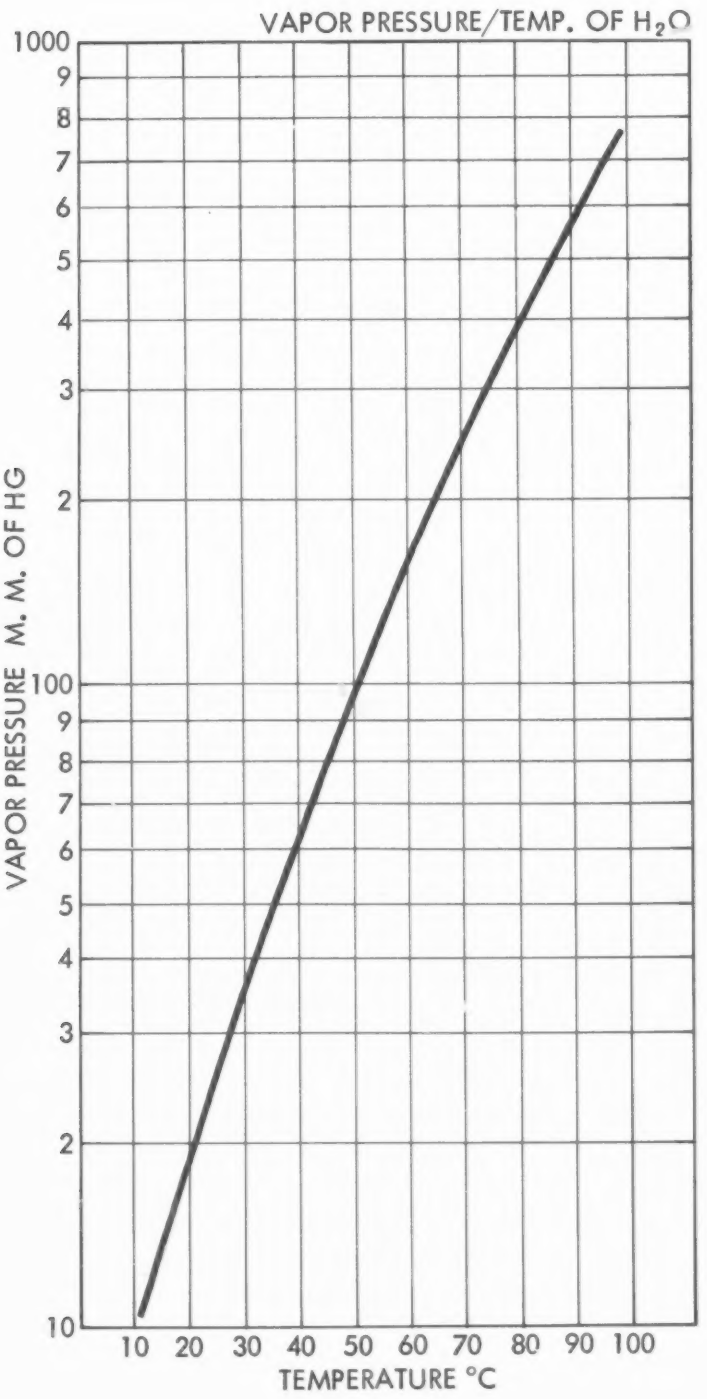
Fig. 20 [Experiment 20]

EXPERIMENT SEQUENCE 21. VAPOR PRESSURE AS A FUNCTION OF TEMPERATURE

This apparatus has been constructed and tested. The liquid is maintained in a cone-shaped cup equipped with a heater. Two 10-watt electrical resistors cemented into the aluminum cup with Sauereisen were used in our apparatus. On tope of the cone is fastened a very light rubber membrane from which the air has been removed. We experimented with balloons but found them to be too heavy for good sensitivity. A condom works very well since the membrane is thin enough to be supported by a pressure difference of 2 mm Hg. The entire apparatus is contained in a bell jar which can be evacuated. With a fixed temperature in the cup the pressure in the bell jar necessary to produce equilibrium (inflation of the bag) is measured.

Because of the large latent heat the temperature of the base will fall when boiling occurs. Care must be taken to assure that equilibrium exists. This can be done by cycling the pressure over a small range around the equilibrium value.

Cyclohexane and tertiary butyl alcohol as well as water are recom-



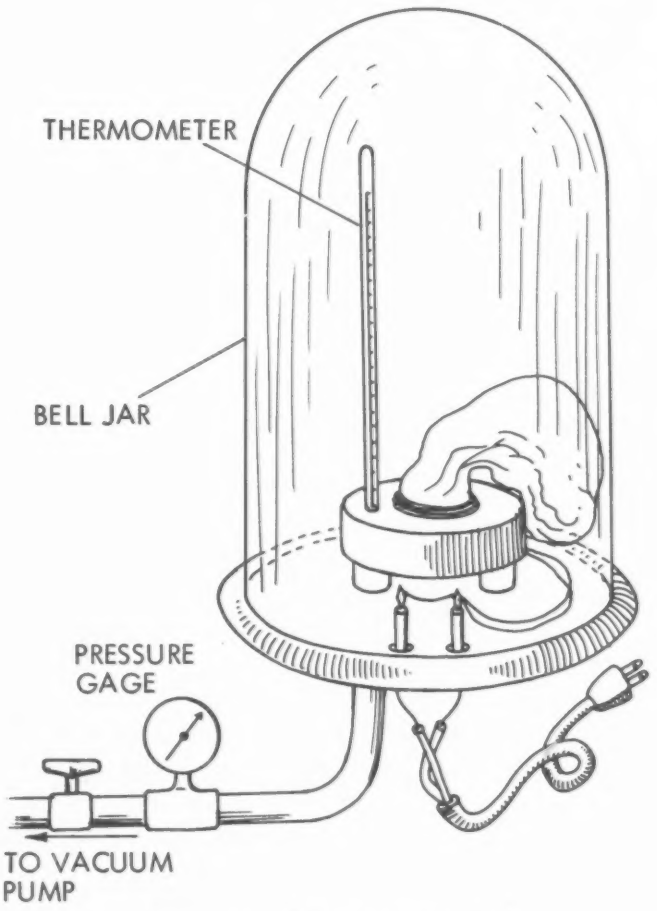


Fig. 21 [Experiment 21]

mended as sample materials. If a thermoelectric cooler were available the curve could be extended downward to the triple point.

The student should plot P(T) and P versus ln T.

EXPERIMENT SEQUENCE 22. CRITICAL-POINT PHENOMENA

A critical-point tube is filled with sulfur hexafluoride (P_c = 37.1 atm, T_c = 45.5°C) and sealed off. A high-intensity lamp is required to observe light scattering at right angles. Because the use of critical-point tubes with students may be hazardous this experiment may be replaced by a demonstration or filmed version. One important variation however is the use of a U tube with the liquid on one side only. The liquid is heated above the critical point and then re-

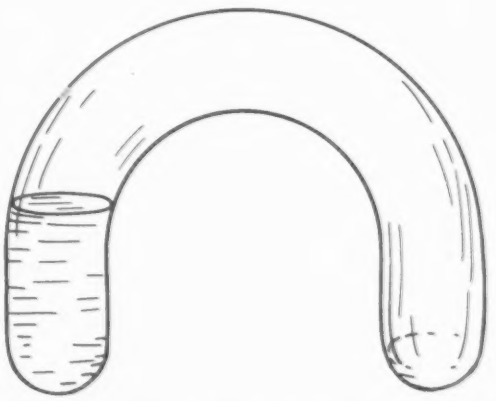


Fig. 22 [Experiment 22]

condensed. It will show a tendency to recondense on the original side, which should provoke some valuable speculation.

EXPERIMENT SEQUENCE 23. SUBLIMATION CURVE

This experiment has not been tried. It is worth doing if a suitable apparatus can be developed. One might, for example, use a device similar to Experiment 21 with a thermoelectric cooling element. However, the solid material will be difficult to return to the reservoir. Suggested working materials are cyclohexane or CCl_3CF_3.

Plots of the data as P(T) and $P = A \ln T + B$ are desired.

A P A R T I C U L A R M O D E L O F M A T T E R

PREFACE

This manuscript is offered as a sample from the monograph "A Particular Model of Matter" to follow "What Can the Matter Be? This material is in draft form; it is intended only to illustrate how the ideas of the earlier monograph can be continued toward more advanced work. Students using material of this kind would be sophomores or juniors. The calculus which appears here involves only simple graphical concepts and could be self-taught or taught as a digression from the text without much difficulty. Much of it is intuitively obvious from the figures. This material is offered in the hope that it will stimulate others to create new curriculum materials.

Dr. Jack A Soules

To begin a description of a container full of gas, examine one of the photographs reproduced in the previous paper, "What Can the Matter Be?" Note that one region of the volume is as likely to contain a particle as any other. In order to assign numbers and measure to this distribution of particles we shall, in imagination, divide the volume V into smaller volumes ΔV and count the number of particles contained in each ΔV. For example, suppose the container is in the form of a cube of side L (Fig. 1). Then we can divide the cube into a large number of smaller cubes each of side ΔL and count the number of particles in each of the small cubes. If the number N of particles is much larger than the number n of small cubes, then the number of particles per small cube will vary around N/n as an average. We can repeat the observation at subsequent times and find that as the gas of particles takes up many configurations, each cell of the volume tends to hold more and more nearly N/n particles on the average. If the cells are made smaller (n larger) the fluctuations become larger but the average behavior is still approached. As the cells are made smaller still the number of particles per cell will be either zero or one depending on whether the cell has "caught" a particle. We can still describe the gas of particles as being, on the average, uniformly distributed over the volume of the container.

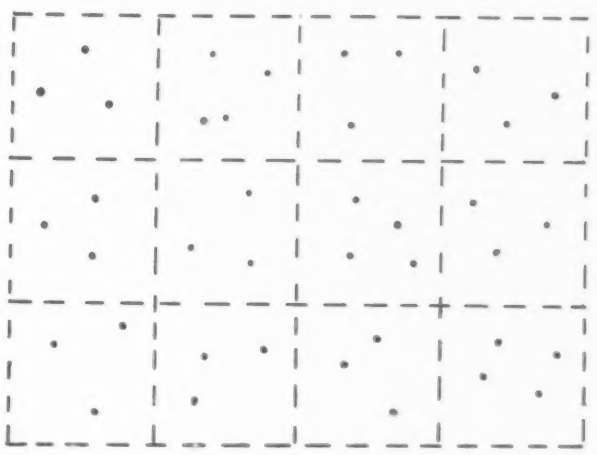


Fig. 1.

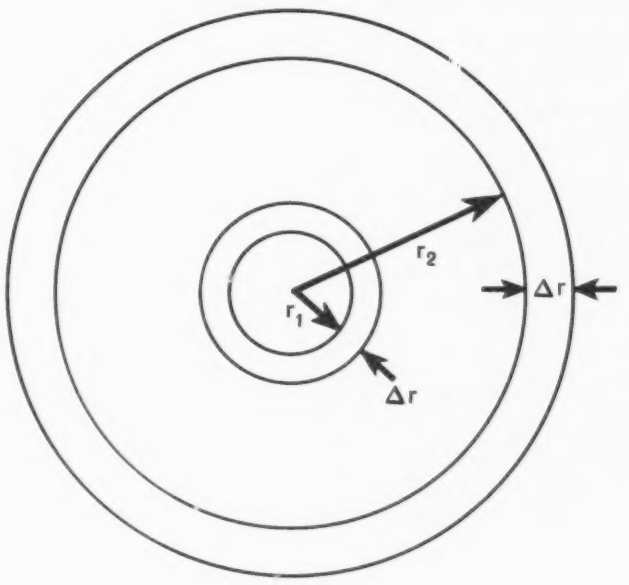


Fig. 2.

If the container is partitioned into slabs, for example parallel to the yz plane, each slab of thickness Δx again shares equally in the total number of particles. One partitioning of the volume which is frequently convenient is to form elements which are spherical in shape (Fig. 2). We select an origin point and then construct a set of concentric spheres of thickness Δr. Even though all of the spherical shells have the same thickness, Δr, they will not have the same volume. In fact, for each shell the volume will be given by

$$\Delta V = 4\pi r^2 \Delta r \qquad (1)$$

The particles, which are on the average distributed uniformly over the volume, are <u>not</u> distributed uniformly over the radius. There are many more particles at large radius from the origin than at small. This is a purely geometric result without significance as far as the behavior of the particles is concerned. However, we shall frequently want to describe the distribution of the particles in terms of a spherical geometry and so will need the expression.

$$\frac{\Delta N}{\Delta r} = \frac{\Delta N}{\Delta V} 4\pi r^2 . \qquad (2)$$

Usually the distribution over the volume will be, on the average, uniform so that the average value of $\Delta N/\Delta V$ is a constant equal to N/n.

We can use this model of the spatial distribution of the gas particles to examine some interesting details. Suppose that we divide the volume into cells in such a way that some cells include the walls of the container within them (Fig. 3). For example, we might have half of the volume of these cells lie on each side of the wall. Evidently the average number of particles per cell will be much less in these cells than in those in the center, in fact, one-half as much. This is the effect of the wall itself, which repels and reflects the particles striking it. We can generalize this simple result into the observation that a region of repulsive force or positive potential energy will have a "number density" lower than that typical of the material as a whole. This will hold true when the particles repel each other strongly also.

If the walls were to attract the particles rather than to repel them, we would expect to get a sort of condensation effect as the number density of particles near the wall increases. Of course, such a wall would remove particles from the gas unless it also had a repulsive force associated with it. A "cold" wall, one which can remove kinetic energy from the particles, would gather particles to itself and clump them there if it exerted an attractive force. In the open region of the volume away from the walls, an attractive force between particles can have a similar effect, especially if some way can be found to remove the kinetic energy. If the particles are becoming attached to one another we shall find some cells with two particles per cell and others with none. If this distribution is still seen when the cells are made smaller, we can deduce that pairing of the particles has occurred. From this crude description of the properties of the spatial distribution of the particles we can get some insight into the "structure" of the material, and in particular into the forces which act between the particles. We shall assume in what follows that the particles of our idealized gas are distributed, on the average, uniformly over the volume available to them.

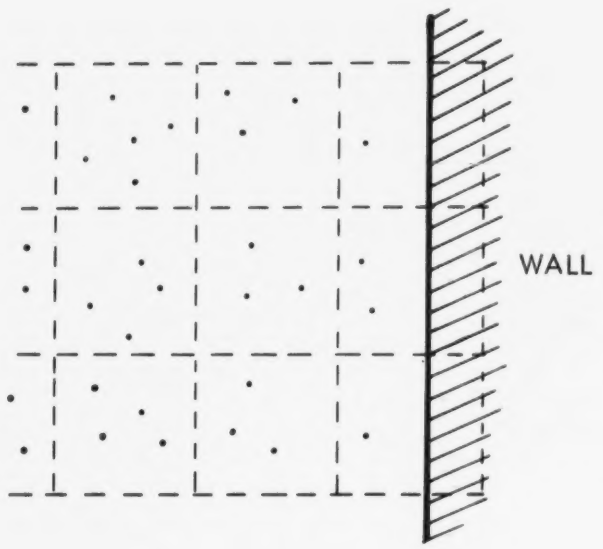


Fig. 3

What can be said of the motions of the particles? We know that the particles collide and exchange momentum and energy. Thus, the description of their motions must include these exchanges. Perhaps the particle motions are distributed at random, that is, perhaps all possible velocities occur. This may be true in fact but it does not reflect very well our knowledge that the total momentum and energy are fixed. We cannot reasonably erect a wall or barrier that limits the velocity of a particle in the way that an ordinary wall confines particles in space. Rather it is the <u>collective</u> velocities of all the particles that are limited. For example, if all of the particles have the same mass M, then the collection is controlled by the equations.

$$M\sum_{i=0}^{i=N} v_{x_i} = \text{const} \qquad (3a)$$

$$M\sum_{i=0}^{i=N} v_{y_i} = \text{const} \qquad (3b)$$

$$M\sum_{i=0}^{i=N} v_{z_i} = \text{const} \qquad (3c)$$

and

$$\tfrac{1}{2}M\sum_{i=0}^{i=N} (v_{x_i}^2 + v_{y_i}^2 + v_{z_i}^2) = \text{const.} \qquad (4)$$

These limitations are much more difficult to express in the real model than were the walls surrounding the volume, V.

Let us construct a new, hypothetical space to describe the motions of the particles. We shall select three Cartesian coordinate axes P_x, P_y, P_z and use each to represent the magnitude of the vector component of the momentum of one particle (Fig. 4). This three-dimensional coordinate space we will call momentum space. A particle with momentum components at a given instant of (3kg m/sec, 4 kg m/sec, 5 kg m/sec) would be represented in the momentum space by a point at (3, 4, 5), that is, at $\sqrt{50}$ momentum units from the origin. The instantaneous motional configuration of the gas is a cloud of points in this space. Notice that the points do not move. The momentum components of a particle remain constant until it has a collision. They then change abruptly, so quickly in fact that the point in momentum space appears to almost jump to another place in the diagram. It is impossible to identify from the momentum space diagram which particles are about to collide. The diagram contains no information about the positions of the particles. When a collision does occur, however, two points appear to jump simultaneously as they exchange momentum and energy. When a particle collides with a wall (Fig. 5) we shall assume that it is reflected away with its component of velocity perpendicular to the wall reversed in direction. Thus a wall reflection causes a point in momentum space to jump across the diagram to a position symmetrically opposite (Fig. 6), keeping for example, its y and z components of momentum and changing the sign of its x component of momentum, for example, from plus to minus. Such a wall collision reduces P_x to zero momentarily, a fact reflected in the way the momentum space point flashes across the diagram through the $P_x = 0$ plane. The momentum space diagram permits us to map the motions of the particles into a geometry problem of the flickering points in momentum space. When there are a large number of particles, and therefore of points in the momentum space, the requirement imposed by the conservation of momentum is not very stringent. All points in the diagram

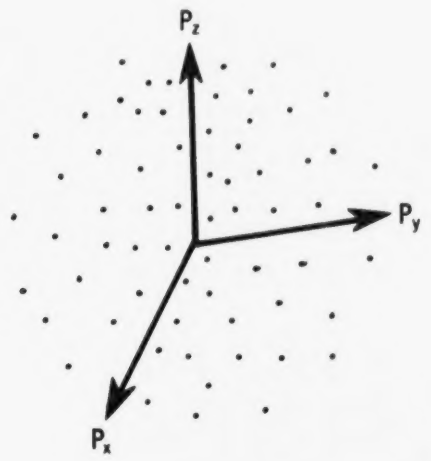


Fig. 4

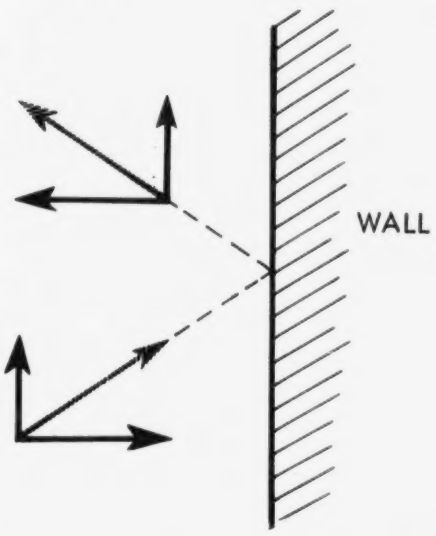


Fig. 5

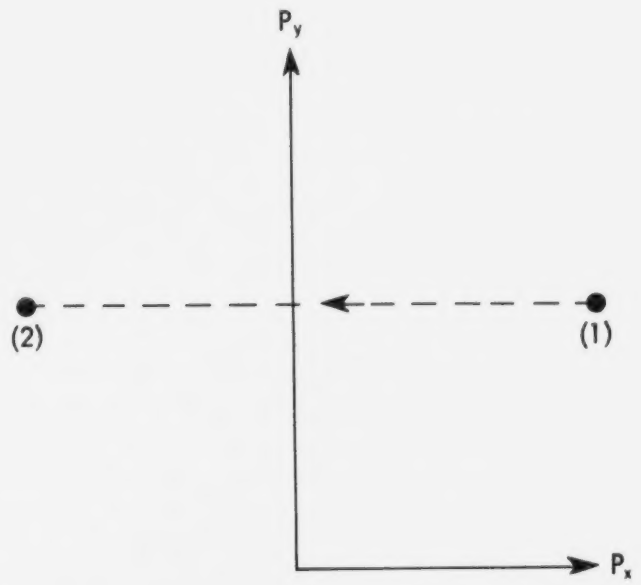


Fig. 6 Reflection from wall perpendicular to x axis.

move in pairs and the two points of a pair maintain a fixed total distance from each of the coordinate planes. That is, since for example in a collision $P_{x_1} + P_{x_2}$ = constant, the sum of the distance of the two points from the $P_y - P_z$ plane is constant. The same condition holds true for the sum of distances from the $P_x - P_y$ plane and from the $P_x - P_z$ plane. This pairing of points is the only requirement imposed by the conservation of momentum principle and leaves the distribution of points over the momentum space quite arbitrary.

An even simpler representation of the gas in a one-dimensional space is possible. This time we select the energy of a particle as the interesting variable. We place a point on a line the proper distance from the origin to represent the energy of one of the particles (Fig. 7) and repeat the process for each of the particles of the collection. Again, as in the case in momentum space, collisions cause a pair of points to be displaced. However, since

$$(E_1 + E_2)_{\text{before}} = (E_1 + E_2)_{\text{after}}, \quad (1.5)$$

the pair of points maintain a constant total distance from the origin. In

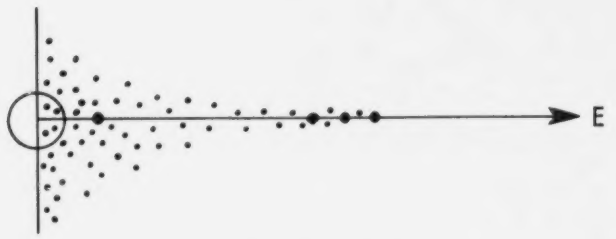


Fig. 7

fact, since the total energy is fixed at some value E, the sum of the distances of all the points from the origin is fixed. This condition, that the sum of the distances of all the points from the origin is a fixed number, can be used to develop a new and exciting property of the collection of particles.

We saw in the description of the gas of particles in real coordinate space that the distribution of points was apparently random, that any part of the volume was as likely to have a particle in it as any other. Let us assume for the moment that this randomization is an inevitable consequence of the collision process and is also true of the distribution of the particles in momentum space and in energy space. However, in these latter two cases, the conservation laws serve as a constraint analogous to the constraint imposed on the spatial distribution by the walls of the vessel. In particular, let us examine what a random distribution of points in energy space looks like, subject to the constraint on the energies of the individual particles E_i, that

$$\sum_{i=0}^{i=N} E_i = E_{\text{total, a constant}} \quad (6)$$

As before, we subdivide the E line into small elements ΔE of equal length and examine the distribution of particles over these elements. We shall form n elements each of size ΔE and number them ΔE_1, ΔE_2, ... ΔE_j, ... ΔE_n. In the jth element we find n_j points. Since all the points together total N in number we have

$$\sum_{j=0}^{j=n} n_j = N_1 . \qquad (7)$$

Furthermore, since the jth cell with n_j points in it contains $n_j E_j$ of the total energy we must also have

$$\sum_{j=0}^{j=n} n_j E_j = E_{total} . \qquad (8)$$

With these restrictions we are free to distribute the points over the elements ΔE any way we like. Some distributions can be made only in a small number of ways. For example, we might choose to put all but one of the particles in the very first element $j = 0$ for which $E_j = 0$. Then the remaining particle would appear in the element $E_j = E_{total}$ which is obviously the element farthest from the origin which we need to consider (Fig. 8). This particular arrangement can be made in just N ways because there are just N ways in which we could choose the particle which goes into E_j element. If we try another distribution, (Fig. 9) say one for which all but two particles are in $E_j = 0$ and the remaining two are in $E_j = \frac{1}{2}E_{total}$, we find we can make it in $N(N - 1)/2$ ways. We can choose one of the two selected particles in N ways and the second in $N - 1$ ways. The number of ways is reduced by half because it doesn't matter which we choose first. Clearly, this distribution can be made in many more ways than the first. Proceeding along these lines, we come quickly to the conclusion that there exists a distribution which can be made in more ways than any other. It is this distribution which we will call the most random or most probable distribution (Fig. 10). If our understanding of the effects of the collisions is correct we expect to find the gas in an energy distribution somewhere close to this most probable one.

How many ways can an arbitrary arrangement of points over the elements ΔE_j be made? A given arrangement in which there are n_0 points in ΔE_0, n_1 points in ΔE_1, and so forth, can be made in $N!/n_0!n_1!n_2!\ldots n_j!\ldots n_n!$ ways.

This is easy to see when we

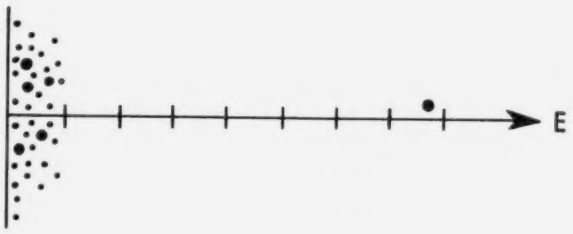


Fig. 8

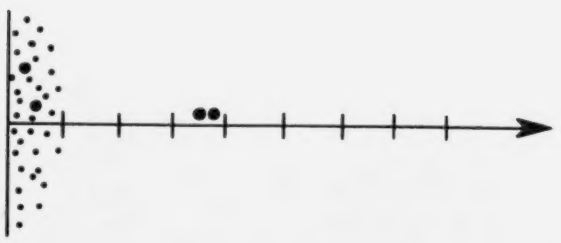


Fig. 9

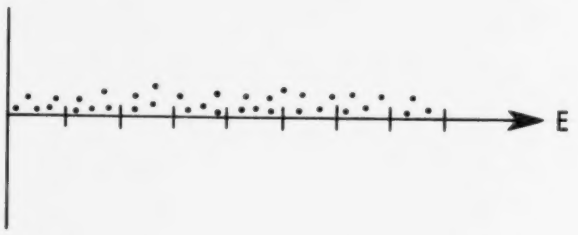


Fig. 10

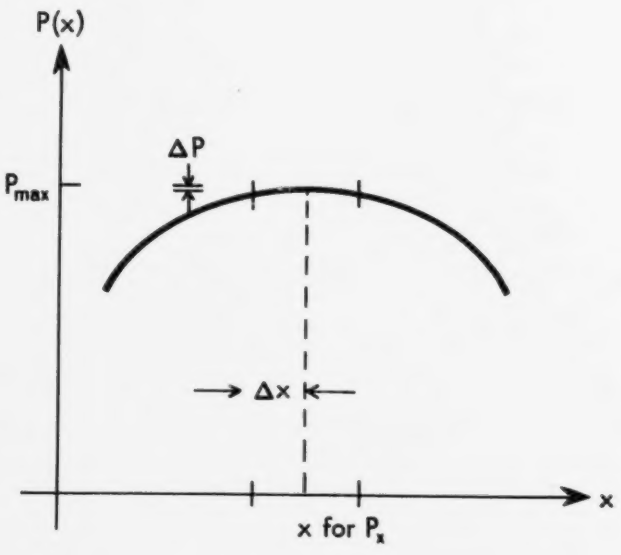


Fig. 11

actually begin to form the distribution; there are N ways we can choose the first point to go in the ΔE_0 element, N − 1 ways to choose the second point, etc. After n_0 points have been selected we realize that the order of selection of these n_0 points is immaterial; any permutation of these n_0 points is, in effect, the same distribution. In multiplying N by (N − 1), (N − 2), etc., we have counted as different $n_0!$ distributions which are in fact all equivalent. Similarly with the n_1 points put in ΔE_1, etc. Therefore we must divide by the numbers $n_0!$, $n_1!$ etc., in order to get a correct count on the total number of different distributions.

The basic task which lies before us is to find the set of numbers n_0, $n_1, \ldots n_j, \ldots n_n$ for which the total number of distributions is as large as possible. This must be accomplished subject to the restrictions on the number of particles and on the energy which are given in Eq. (7) and (8). We could use Eq. (7) to solve for n_0 in terms of N and the remaining n_j and then substitute this in the leading term of Eq. (8). Eq. 8 could in turn be solved for n_1 in terms of E_{total} and N and that result substituted in the distribution expression. However, the distribution expression is in the form of a product of factorials, and if we were to eliminate n_0 and n_1 by substituting these long sums, the algebra would become very messy indeed. We choose instead to follow a variation technique developed by the French mathematician Lagrange. Let us write the count of distributions as a function of the many variables n_j, calling $P(n_0, n_1, \ldots n_j, \ldots n_n)$ the "distribution function." We have

$$P(n_0, n_1, \ldots n_j, \ldots n_n) = \frac{N!}{n_0! n_1! n_2! \ldots n_j! \ldots n_n!} \qquad (9.a)$$

$$= \frac{N!}{\prod_{j=0}^{j=n} (n_j!)} \qquad (9.b)$$

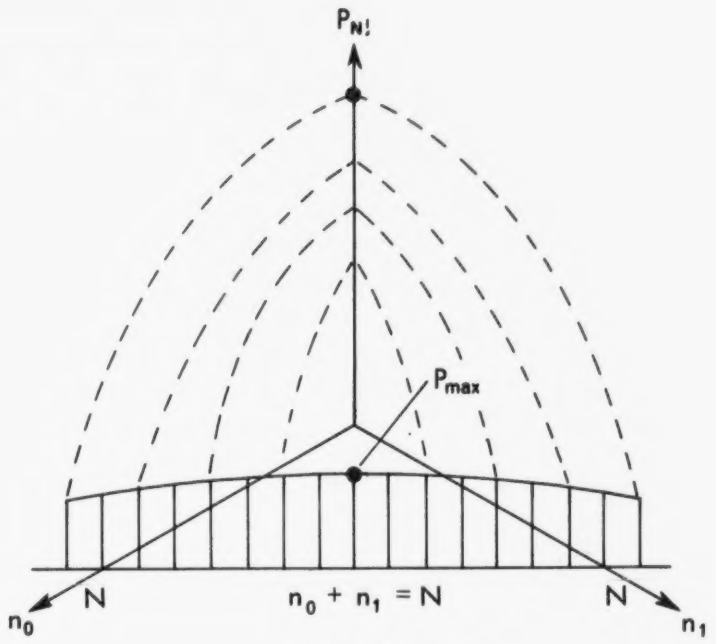


Fig. 12

The mathematical task is to maximize the number P by appropriate selection of the various numbers n_j. In mathematical terms, a function is maximized if any small variation of the independent variable reduces the value of the dependent variable. Since at a maximum the dependent variable decreases regardless of whether the independent variable increases or decreases we have the general conditions for a maximum[1]

$$\frac{\Delta y}{\Delta x} = 0 \text{ and } \frac{\Delta^2 y}{\Delta x^2} < 0. \qquad (10)$$

In Fig. 11 we illustrate for a function P(x) the behavior of P near its maximum. We can imagine the function P constructed in an m dimensional space somewhat as illustrated in Fig. 12. P is small for large n's and large for small n's. However, this simple statement fails to take account of the requirement that the sum of the n_j's must be N. This additional condition describes a "surface" in multidimensional n_j space and it is over this surface that we must look for the maximum of P. We cannot draw these geometric figures in multidimensional

[1] We rule out pathological cases such as functions with cusps, discontinuous functions, etc.

spaces but we can give an idea of their properties in a three-dimensional sketch. We see, for example, that the maximum value of P occurs for $n_0 = n_1$ when the condition $n_0 + n_1 = N$ is imposed.[2] This is a general result. For the complete set of cells $n_0, n_1, \ldots, n_j, \ldots n_n$, the maximum of P occurs when

$$n_0 = n_1 = n_2 = \ldots = n_j = \ldots = n_n \tag{11}$$

This is a purely mathematical result and does not yet meet the requirements of our physical situation, for we still have to impose the condition that $\Sigma n_j E_j = E_{total}$. This condition is also a surface in the multidimensional n space. The two conditional surfaces, $\Sigma n_j = N$ and $\Sigma n_j E_j = E_{total}$, intersect in a surface whose dimensionality is $n - 2$ and it is on <u>this</u> surface that we wish to maximize P.

It is much easier to perform the mathematical manipulations for maximizing P than it is to draw or even to imagine the geometric figures. A complication occurs in that factorial functions are not familiar ones for analytic manipulation. Therefore, let us pause a moment to examine some properties of these functions. If we plot n! against n we find that it increases very rapidly (Fig. 13). In fact almost as rapidly as n^n. Stirling developed an excellent approximation to the factorial function, expressing it in terms of common analytic functions. Stirling's approximation is

$$n! \cong \sqrt{2\pi n}\,\frac{(n)^n}{e}, \tag{12}$$

which is frequently written in logarithm form as

$$\ln n! \cong \frac{1}{2}\ln(2\pi n) + n \ln n - n. \tag{13}$$

[2]The "surface" of restraint becomes a line in 2 dimensional space.

Since the logarithm of P increases monatonically with P, we can as well maximize ln P as to maximize P; the utility of Stirling's approximation encourages us to maximize ln P instead of P. From Eq. (9) and (13) we have

$$\begin{aligned}\ln P(n_0, n_1, \ldots, n_j, \ldots n_\eta) &= \ln N! - \ln n_0 - \ln n_1! - \ldots - \\ &- \ln n_j! - \ldots - \ln n_m! - \\ &= -\ln N! - \sum_{j=0}^{j=n} \ln\ n_j! \qquad (14)\\ &\cong \tfrac{1}{2}\ln(2\pi N) + N \ln N - N \\ &- \sum_{j=0}^{j=n} \tfrac{1}{2}\ln(2\pi n_j) - \sum_{j=0}^{j=n} n_j \ln n_j \\ &+ \sum_{j=0}^{j=n} n_j \qquad (15a)\\ &= \left(\tfrac{1}{2}\ln 2\pi N + N \ln N\right) - \\ &- \left[\sum_{j=0}^{j=n} \tfrac{1}{2}\ln(2\pi n_j) + \sum_{j=0}^{j=n} n_j \ln n_j\right] \qquad (15b)\end{aligned}$$

It is a well-known result from the elementary calculus that $\Delta(\ln y) = \Delta y/y$. Applying this to P, and to each of the n_j in turn, yields

$$\frac{\Delta P}{P} = -\sum_{j=0}^{j=n}\frac{\Delta n_j}{4\pi n_j} - \sum_{j=0}^{j=n}\left[\frac{n_j}{n_j}\Delta n_j + (\ln n_j)\Delta n_j\right] \tag{16a}$$

$$= -\left[\sum_{j=0}^{j=n}\left(\frac{1}{4\pi n_j} + 1 + \ln n_j\right)\Delta n_j\right]. \tag{16b}$$

The restrictive conditions, (7) and (8) must now be rewritten in terms of the Δn_j. From (7) we have

$$\sum_{j=0}^{j=n}\Delta n_j = 0 \tag{17}$$

$$\sum_{j=0}^{j=n} E_j \, \Delta n_j = 0. \qquad (18)$$

In order to combine Eq. (17) and (18) with Eq. (16) we must take account of the different dimensionality of the various expressions. That is, whereas Eq. (16) and (17) are expressions in pure numbers, Eq. (18) is an expression for energy. We simply generalize (17) and (18) by writing

$$\alpha \sum_{j=0}^{j=n} \Delta n_j = 0 \qquad (19)$$

and

$$\beta \sum_{j=0}^{j=n} E_j \Delta n_j = 0, \qquad (20)$$

where α and β are arbitrary multipliers. Because this method of imposing the restraining conditions in the maximum problem was developed by Joseph Louis Lagrange, we call the numbers α and β Lagrange multipliers.

When combined with (19) and (20), Eq. (16) must now be made to yield a maximum. That is, $\Delta P/P$ must vanish when the set of numbers n_j is properly chosen. The numbers Δn_j are perfectly arbitrary. They represent small variations in the n_j near the maximum. Combining Eq. (16) with (19) and (20), we have

$$0 = -\left[\sum_{j=0}^{j=n} \left(\frac{1}{4\pi n_j} + 1 + \ln n_j + \alpha + \beta E\right) + \Delta n_j\right]. \qquad (21)$$

This result must hold for all arbitrary Δn_j so that for <u>each</u> n_j we must have

$$\frac{1}{4\pi n} + 1 + \ln n_j + \alpha + \beta E_j = 0_1. \qquad (22)$$

The argument which leads to Eq. (22) is simple. If for any n_j, say $n_{1\,0}$, Eq. (22) does <u>not</u> hold, we have only to make $\Delta n_{1\,0} \neq 0$ and all of the other

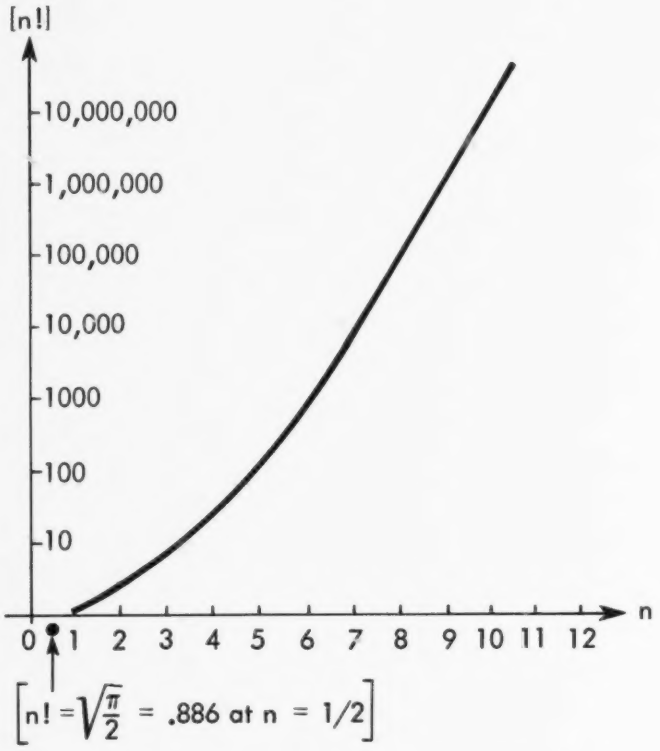


Fig. 13 Plot of Stirling approximation

$\Delta n_j = 0$ to get a contradiction in Eq. (21). Therefore Eq. (22) holds for <u>all</u> j.

The only approximation in our calculation so far was that of Stirling which was chosen for mathematical convenience. The error introduced by Stirling's approximation is less than 1% when n_j is 10. If we now discard the term $1/4\pi n_j$ in Eq. (22), we introduce an error which is again less than 1% for $n_j = 10$ or more. We are left with a simple expression for n_j as a function of E_j which is valid for numbers n_j as large as 100 or more, namely

$$\ln n_j = -(\alpha + 1) = \beta E_j \qquad (23)$$

which is equivalent to

$$n_j = \exp -(\alpha + 1) \exp -(\beta E_j). \qquad (24)$$

In words, the distribution of particles which can be made in the largest number of ways consistent with the conservation of particles and the con-

servation of energy is an exponential distribution. We shall not take the trouble to examine the actual number of ways in which this distribution can be made. For N even as large as 100, P_{max} is astronomically large. If even a few particles are moved to other cells so that the distribution varies only slightly from the optimum exponential form, the number P (n_0, n_1 ...) drops to 1/10 or less of its maximum value. The maximized distribution is a very well-defined state of the particles.

We have devoted an inordinate amount of effort to the development of this result because it stands at the very center of the physics of many bodies. If the interactions are of such a kind that the system tends to randomize itself, then the energy will eventually be distributed over the particles in an exponential way. There will be many particles of small energy and only a few particles of large energy. The exponential result itself is a mathematical outcome from the factorial functions which appear in the permutation counts. As we count the number of possible arrangements, we find that the order in which particles are selected for a given energy is arbitrary. Therefore, we must divide the total count by each of the n_j! It is these n_j! terms which, coupled with the $\Sigma n_j E_j = E$ condition gives rise to the term $\exp -(\beta E_j)$.

We have used two of the conservation principles available to us, conservation of particles and conservation of energy, in obtaining Eq. (24). We have not yet involved the conservation of momentum. Therefore, although all possible distributions of the particles in real space and in momentum space must satisfy Eq. (24), not all distributions which satisfy Eq. (24) are possible. That is, Eq. (24) is a necessary, but not a sufficient, condition for the distribution. In order to develop the details of the distribution further, we turn again to an examination of the points representing the particles in momentum space.

Since the particles are free, their momentum and energy bear a simple relationship to one another, namely

$$E_i = \tfrac{1}{2} m v_i^2 = \frac{\tfrac{1}{2} m^2 v_i^2}{m} = \tfrac{1}{2} \frac{P_i^2}{m}. \qquad (25)$$

The quantity P_i^2 is the square of the radial distance from the origin to the point representing the ith particle in momentum space. Equation (25) expresses the fact that the number of points per unit volume in momentum space must decrease exponentially with the square of this distance (Fig. 14).

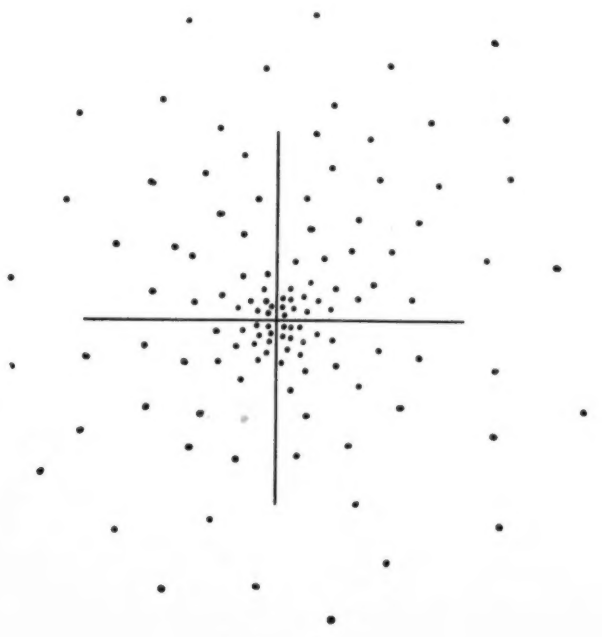


Fig. 14.

Further statements about the distribution of points in momentum space require a detailed examination of the mechanics of the collision process. However, our understanding of the way pairs of points exchange momentum in a collision can lead us to insight into the distribution. Points involved in a collision move rapidly across the momentum space diagram, but always in such a way that as one moves, say, left toward the P_x axis the other moves to the right, away from the P_x axis, keeping the total x component of momentum fixed. If we imagine a point to be sweeping out a small cylindrical tunnel as it moves, it is

not surprising that the volume of each pair of tunnels is fixed. Liouville was able to generalize this observation into the theorem that all volumes of the momentum space contain, on the average, an equal density of points, subject only to the $\exp(-\beta p^2)/2m$ factor. With the addition of Liouville's principle, which summarizes the conservation of momentum conditions in momentum space, we can proceed to complete the description of the distribution function.

We shall write the distribution of points in momentum space to be[3]

$$\Delta N_k = A \exp \frac{(-\beta P^2)}{2m} \Delta Px_k \Delta Py_k \Delta Pz_k, \quad (26)$$

[3]The constant A in Eq. (26) replaces the term exp - $(\alpha + 1)$ of Eq. (24).

where ΔN_k is the number of points in the small momentum space volume element ΔVp_k. ΔVp_k is the kth cubical volume element, whose sides are $\Delta \vec{Px}_k$, $\Delta \vec{Py}_k$ and $\Delta \vec{Pz}_k$, and it is located at Px_k, Py_k and Pz_k. It is frequently more convenient to express the distribution in terms of the number of points in a spherical shell of radius $\vec{Pk}$. In this case

$$\Delta N_k = A \exp -\frac{(\beta \vec{Pk}^2)}{2m} 4\pi \vec{Pk}^2 \Delta \vec{Pk}. \quad (27)$$

We must now apply the particle conservation principle and the energy conservation principle to evaluate the constants A and β, and so determine explicitly the distribution of points in momentum space.